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*The Principles of Diffusion, their Analogies and Applications.*

A Lecture delivered before the Chemical Society on June 6th, 1918.

By HORACE T. BROWN, LL.D., F.R.S.

How it comes about that one who is neither physicist nor mathematician should have the temerity to address you on the subject I have chosen for my lecture requires a few words of explanation.

I was perforce led to the study of the phenomena of diffusion some twenty years or so ago when investigating the photosynthetic processes which go on in the green organs of plants. A serious difficulty occurred in finding an explanation of the mode by which the assimilatory centres of a leaf can be supplied with the highly dilute carbon dioxide of the air with sufficient rapidity to account for the observed rate of increase of carbohydrates in a leaf lamina placed under favourable conditions of insolation.

Some idea of the required magnitude of this gaseous flow may be gathered from the fact that when a leaf is actively assimilating, it may happen that its surface is taking in atmospheric carbon dioxide more than half as fast as an equal area of a concentrated solution of alkali hydroxide would do if submitted to a constantly renewed current of air with the same carbon dioxide content.

This would be a surprising fact even if we regarded the whole surface of the leaf as being permeable to atmospheric carbon dioxide, but we now know with certainty that the leaf cuticle is impervious to carbon dioxide at partial pressures considerably above those at which it occurs in the air, and that the whole of the gaseous exchanges incident to assimilation take place by free diffusion through the stomata, minute apertures in the cuticle which only represent from about 1 to 3 per cent. of the total surface area of the leaf. Hence it follows that these minute openings must have the power of drinking in atmospheric carbon dioxide at a rate about fifty times greater than apertures of similar dimensions would do if they were filled completely with a constantly renewed solution of alkali hydroxide.

This led me to an experimental investigation of the laws of diffusion as applied to the passage of gases through small apertures and multiperforate septa, and ultimately to a complete explanation of the mode by which the diffusive flow can be accelerated by such structures as we find in the leaf, without postulating anything inconsistent with the well-established laws of diffusion; in fact, if

the exact conditions are defined, the degree of efficiency of such a mechanism can be deduced from those very laws.

It is to these and certain other cognate phenomena that I wish to direct your attention this evening, in the hope that my remarks may stimulate further inquiry into a subject of considerable interest, which has many applications in various directions.

That chemists generally in this country have paid far too little attention to diffusion phenomena, and to the important part which they play in many departments of chemistry and biology, is sufficiently evident from the scanty treatment which they have received in the majority of our text-books. This is the more remarkable and less excusable, since the very foundations of our knowledge of the subject were laid down by Thomas Graham, of pious memory, one of the founders and the first President of this Society. If chemists had rendered themselves more familiar with such questions, less surprise would have been expressed when Nernst, as recently as 1904, stated what ought to have been a self-evident proposition, that determinations of the velocities of reactions taking place at the boundaries of heterogeneous systems may be entirely vitiated if we fail to take into account diffusivity as a possible limiting factor.

In this connexion, I should like to refer as briefly as possible to some experiments which I made at the very outset of my inquiries, since they well illustrate this proposition of Nernst.

When a current of air containing any constant proportion of carbon dioxide up to about 18 or 20 parts per 10,000 is caused to move in a turbulent stream of known velocity over the free surface of a normal solution of sodium hydroxide, the temperature being maintained constant, the rate of absorption of carbon dioxide per unit area increases with the speed of the current until a linear velocity of about 260 metres per hour is reached. As long as the other conditions are unaltered, any further increase in the velocity of the air current is unattended by any change in the rate of absorption, the concentration of the carbon dioxide at the immediate boundary of the two surfaces having then attained its maximal value. Until this point is reached, gaseous diffusion is still playing some part in the reaction. That there is no corresponding limitation of the reaction in the liquid itself is shown by the fact that the rate of absorption is not influenced by any further stirring of the solution other than that produced by the air-current passing over it.

Under these conditions, the rate of absorption of the carbon dioxide per unit area of liquid surface varies directly with its partial pressure, and so exact is this relation that it has formed the

basis of a very accurate method for determining the amount of carbon dioxide in the air, which has the advantage that it is quite unnecessary to measure the volume of air employed.

The following table illustrates the degree of accuracy attainable by measuring the rate of absorption per unit area.

The first column shows the carbon dioxide content as given by passing measured volumes of air through a Reiset apparatus, whilst the second column gives the corresponding values deduced from the rate of surface absorption by a known area of the absorbent liquid over which unmeasured volumes of air have been passed in a turbulent stream at a sufficient velocity to produce the maximal effect. The results are given in parts per 10,000 of air reduced to normal temperature and pressure.

TABLE I.

(1).	(2).	Differences.
0.04	0.04	0
0.19	0.19	0
0.56	0.57	+0.01
1.08	1.08	0
1.15	1.21	+0.06
3.21	3.30	+0.09
3.36	3.30	-0.06
4.58	4.41	-0.17
4.89	4.93	+0.04
6.75	6.72	-0.03
7.65	7.50	-0.15
8.64	8.23	-0.31
12.53	12.40	-0.13
17.94	17.74	-0.20

The researches of Graham on the diffusion of gases, commenced in 1829, and continued at intervals up to 1863, are so well known that I need only make a passing allusion to them. They were carried out for the most part with an intervening septum of some porous material, such as plaster of Paris or thin plates of compressed graphite. When the gases communicated through such narrow channels or pipes he was led to a certain generalisation, which in his own words was as follows:

"The diffusion, or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being in the case of each gas inversely proportional to the square root of the density of that gas."

Such results had, of course, only relative values, and Graham clearly saw that absolute values could only be ascertained by allowing the gases to mix through a wide opening by free and unobstructed diffusion. It was only at a much later period that he

commenced any systematic experiments in this direction. He briefly described these in the concluding section of his paper of 1863 on the "Molecular mobility of gases" (*Phil. Trans.*, 1863, 385) with the sub-heading "Interdiffusion of gases without any intervening septum." Beyond showing that whilst a portion of carbon dioxide can diffuse through air at the rate of 7.3 cm. per minute, whilst a sensible portion of hydrogen travels in the same time about five times as far, these experiments did not lead to much, and the numerical results do not lend themselves to a determination of the coefficients of diffusion. Some seven or eight years afterwards, however, they served as a starting point for Loschmidt and his school in establishing a consistent theory of gaseous diffusion.

Long prior to this period Graham had been investigating the diffusion of liquids by his "open jar" method, and in his Bakerian Lecture of 1850 he described a large number of experiments on the comparative diffusivity of different substances in solution. His general conclusions were that, whilst every substance has its own particular velocity of diffusion, the actual rate of transference in solutions of the same substance depends on its initial concentration and on the temperature. Other things being equal, the amount of salt diffused in a given time is very nearly proportional to this initial concentration, and increases with the temperature.

Graham made no attempt to formulate any general law connecting the three variables time, concentration, and space traversed by the diffusate, but his observations fortunately attracted the attention of A. Fick, of Zurich, who, five years afterwards, in 1855, succeeded in developing from them a fundamental law for the operation of diffusion in a single element of space.

Fick's law of diffusion, like Ohm's law at an earlier date, was derived from the principles enunciated in 1822 by Fourier in his celebrated work on the Analytical Theory of Heat—principles which have been found applicable to so many diverse yet analogous sets of phenomena.

Lord Kelvin justly described this treatise of Fourier as a great mathematical poem. Although its beauty and magnificence can perhaps only be adequately and fully appreciated by the mathematician, it is a work of genius which cannot fail to excite the wonder and admiration even of those who, like myself, have not the requisite mathematical knowledge to follow it in all its details.

It was no doubt the ninth chapter of this treatise, dealing with the linear diffusion of heat in rigid substances, which gave Fick the desired clue to his law of diffusion.

Fourier had shown that if we imagine a plane lamina of conducting material with parallel faces, one of which is kept at a constant temperature  $\mathfrak{S}_1$ , and the other at a lower temperature  $\mathfrak{S}_2$ , and sufficient time has elapsed to establish a permanent flow of heat between the two surfaces, then the quantity of heat  $Q$ , flowing through the lamina in a given time  $t$ , will be directly proportional to the temperature difference  $\mathfrak{S}_1 - \mathfrak{S}_2$  of its two surfaces.  $Q$  must also be directly proportional to  $A$ , the area of the lamina, and inversely proportional to its thickness  $x$ , so that we get the following general expression for the steady condition of the flow of heat:

$$Q = k \frac{\mathfrak{S}_1 - \mathfrak{S}_2}{x} At.$$

in which  $k$  is a quantity dependent on the nature of the substance and representing its conductivity.  $k$  is a constant if the conductivity does not vary with the temperature, and may be defined as numerically equal to the quantity of heat which will flow through unit area of a lamina of unit thickness in unit time, when there is unit difference of temperature between the two faces.

If the lamina is supposed to have an infinitely small thickness  $dx$ , and there is an infinitely small temperature difference between its two faces, the above expression becomes

$$Q = \frac{d\mathfrak{S}}{dx} A \cdot dt.$$

$\frac{d\mathfrak{S}}{dx}$  is the "gradient of temperature" at any point, so that the flow through unit area per unit time is numerically equal to the conductivity multiplied by the temperature gradient.

It is the particular merit of Fick that he was the first to express the idea that in all probability diffusion follows the same law, and that, *mutatis mutandis*, it is applicable to the transference of a solute in its solvent, just as Ohm had found it applicable to the flow of electricity in a conductor, the concentration of the solute being in one case the analogue of temperature and in the other of electrical potential.

Proceeding exactly according to the model of Fourier's mathematical development of a linear flow of heat, and assuming that in a diffusive column concentration gradient corresponds with temperature gradient, Fick arrived at the conclusion that when a solute diffuses in an axial direction along a column of constant cross-section, that is, one which is cylindrical or prismatic, the fall of concentration  $p$ , in any infinitely thin layer, at a distance  $x$  from



any point of reference in the column, should in a given time  $t$  satisfy the partial differential equation.

$$\frac{\partial \rho}{\partial t} = -k \frac{\partial^2 \rho}{\partial x^2}.$$

In this formula  $k$  represents the coefficient of diffusivity which, subject to certain limitations, presently to be referred to, is constant for any given solute and solvent as long as the temperature does not vary. It is the exact analogue of Fourier's coefficient of heat conduction.

To quote Fick's own words: "According to this law, the transfer of salt and water occurring in a unit of time between two elements of space with differently concentrated solutions of the same salt must, *ceteris paribus*, be directly proportional to the difference of concentration, and inversely proportional to the distance of the elements from one another."

The law should hold good for any case of diffusion in which the lines of flux are parallel to each other, whether the condition of steady flow has been attained or not, but, owing to the difficulties attending the calculation of a sufficient number of values for the development of the integrals of the equation for special cases, Fick sought the requisite experimental proof in an examination of the distribution of density in a diffusive column which had attained the state of dynamic equilibrium. Under these conditions, the diffusive flux no longer alters the concentration in the space through which it passes, since each infinitely thin layer is receiving as much salt on one side as it is passing on to the next similar layer in juxtaposition.

The above fundamental equation can be shown to contain the proposition that when such a steady condition has been reached, the differences of concentration of any two pairs of strata in the column must be proportional to the distances of those strata, so that the decrease of concentration measured along the axis of the column ought to vary as the ordinates of a straight line.

The experimental method by which Fick attempted to verify this deduction was a somewhat crude one, but the results as a first approximation were found to be in fair accord with theory. Since his time many observers have introduced more refined processes for determining the progressive variations of concentration in a static column, based on optical, chemical, and electrical methods. By far the most satisfactory of these is due to Weber, who in 1879 made use of the fact that the *E.M.F.* developed between two electrodes of zinc or two of copper, immersed respectively in solutions of zinc sulphate and copper sulphate, can be used for measuring with great exactness the concentration at the boundary surface

in contact with the electrodes. The results in every way confirmed the accuracy of Fick's law.

Graham in his last paper on liquid diffusion, published in the *Philosophical Transactions* for 1861, recorded the results of a further series of experiments in which he used an improved method of 'jar-diffusion,' which enabled him to ascertain the degree of concentration of a salt in progressive layers of the diffusion column of a certain definite thickness. He does not refer to the important generalisation of Fick, which was apparently unknown to him, so that his conclusions as regards diffusion velocities are only of relative and qualitative importance. It was not until Stefan in 1879 had submitted these latest results of Graham to mathematical treatment that they were shown to be, on the whole, in accord with Fick's law. That the desired experimental verification should in the first place have been forthcoming from studies on hydro-diffusion rather than from those on gaseous diffusion is not surprising, since, in the latter instance, the molecular interpenetration, which is the essence of the process, takes place with far greater rapidity, and the difficulties in preventing mass movements are correspondingly increased.

Satisfactory proof that the progress of gaseous diffusion can also be expressed by Fick's law was first given by Loschmidt in 1870, the partial pressures of the interpenetrating gases being equivalent to the 'concentration' in hydro-diffusion. As might be expected, the law also holds good for the diffusion of vapours proceeding from the surfaces of volatile liquids.

A full and complete theory of gaseous diffusion from the kinetic point of view has still to be formulated, although so much has been done in this direction by mathematical physicists that there is a reasonable hope that all the observed phenomena will ultimately be deducible from a completed dynamic theory. Be that as it may, however, Fick's law or Fourier's law, whichever we may choose to call it, is one that enables us to solve nearly all the problems met with in practice, and it has the advantage that it is quite independent of any hypothetical assumptions as to the nature, constitution, or molecular condition of the substances taking part in diffusion, provided no dissociation occurs during the process. It merely gives in a compendious and useful mathematical form the experimental relations which exist between the three variables concentration, time, and space traversed in such a manner as to admit of ascertaining the state of the system at any given stage. Like the Phase Rule, it is a theorem which would still remain true even in the unlikely event of our present kinetic and molecular theories being radically modified or entirely abandoned.

The essence of Fick's law is that the 'driving forces' which cause the transference of a substance from regions of high to regions of low concentration are proportional to the concentration gradient.\*

Fick's fundamental law, like all other "laws," has its limitations and must be regarded merely as a close approximation to the truth, and subject to correction as our knowledge increases. As it stands it may be compared with the uncorrected gas law of Boyle connecting pressure with volume. It assumes, for instance, that the coefficient of diffusion,  $k$ , at a given temperature is constant and independent of the concentration, which is certainly not strictly correct.

In his "Kinetic Theory of Gases," O. E. Mayer, in attempting to deduce the theoretical formula of gaseous diffusion from the kinetic considerations of Maxwell and Stefan, indicates that whilst the dynamical theory is in accordance with observation as far as the influence of temperature and pressure is concerned, his dynamic formula suggests that  $k$ , the diffusivity coefficient, ought to vary slightly with the number of molecules of one or the other kind of gas in unit volume of the mixture; that is to say, it ought to assume a somewhat different value in different parts of a diffusive column, dependent on the ratio of mixture.

Small progressive variations of this kind have been recently recorded by Jackmann, Deutsch, Schmidt, and Lonius for the free interdiffusion of various pairs of gases, but it is questionable whether the very small differences recorded are not within the limits of experimental error (see Jean's "Dynamical Theory of Gases," p. 334). Moreover, these experiments were necessarily conducted with the two gases initially at equal pressures, and therefore containing the same number of molecules per unit volume. O. E. Mayer has pointed out that these are not the best conditions for ascertaining if  $k$  varies with the ratio of mixture, and that we ought to employ gaseous mixtures containing only small masses of one of the constituents.

\* It is somewhat surprising that the phenomena of osmotic pressure have not been often regarded from this point of view.

It is as legitimate to speak of the concentration of the *solvent* in a solution as the concentration of the *solute*, both are expressed by  $\frac{\text{mass}}{\text{volume}}$ . As the concentration of the solute increases that of the solvent diminishes. When a solution and the pure solvent are separated by a membrane impervious to the solute the inequality of "concentration" of the solvent on either side of the membrane must necessarily result in a diffusion current passing across the membrane from the region of high concentration of the solvent to regions of low concentration, that is, from the pure solvent to the solution. It is this process which gives rise to the "osmotic pressure."

During a certain stage of my work, I have been able to realise these conditions by determining the rate of the diffusive flow of atmospheric carbon dioxide, at a partial pressure of about  $3/10,000$  of an atmosphere, along a column of air after the static condition had been induced by introducing a perfect absorber of the carbon dioxide at one end of the tube.

If the coefficient of diffusivity for the system carbon dioxide-air is appreciably influenced by the ratio of mixture, these are just the conditions under which one would expect indications of it.

In these experiments, and in others made by determining the rate of flow through apertures of known dimensions, no positive evidence of any such differences was forthcoming (see Brown and Escombe, *Phil. Trans.*, 1900, [B], 193, 241, 269).

In the phenomena of hydro-diffusion there is more convincing evidence that the value of  $k$  appreciably varies with the concentration, but until we have more accurate determinations of the coefficients of diffusivity of solutes than at present, this and other small disturbing influences, such, for instance, as those due to volume changes induced by the progressive dilution of the diffusate, cannot be evaluated with certainty.

Meanwhile, Fick's law is a very good approximation and sufficient for all ordinary purposes. It only requires correction in the same manner as does Fourier's law in the theory of heat-conduction: "as there the quantity of internal conduction slowly diminishes as the temperature rises, so here the quantity of the diffusion gradually sinks to smaller values as the concentration increases; Fick's hypothesis expresses the course of diffusion with only the same accuracy with which Fourier's elementary law represents the process of the conduction of heat in rigid bodies" (Weber).

I must now pass on to the consideration of some concrete examples of diffusion in certain typical and well-defined systems.

I have already referred to some of the conditions which exist in a diffusion column of cylindrical or prismatic shape when the concentrations of the diffusing substance are maintained at constant but unequal values at its two faces for a sufficient length of time to induce the steady condition of flow from one face to the other. In such a system, equal amounts of the diffusate must necessarily pass across each cross-section in equal intervals of time, and the fall of concentration of the diffusate will be uniform; that is to say, if the densities or concentrations are plotted against the corresponding distances of the cross-sections from the point of origin, the slope or gradient of density will be represented by a right line

A A'

the steepness of which is inversely proportional to the total length of the column.

If the concentration at one face is represented by  $\rho$ , that at the other face by  $\rho_1$  some value which is less than  $\rho$ , and the length of the column by  $L$ , then at constant temperature the magnitude

$Q$  of the flux will vary directly as the gradient  $\frac{\rho - \rho_1}{L}$ .  $Q$  will also

be directly proportional to the area of the cross-section of the column, to the coefficient of diffusivity  $k$ , and to the time  $t$ .

If consistent units are employed, the diffusive *efficiency* of the system will be represented by the equation

$$Q = k \frac{\rho - \rho_1}{L} At.$$

In such a static system the stream lines of the flux will be represented by an infinite number of straight lines drawn parallel to the axis of the column. On the other hand, every cross-section of the column corresponds with a surface of equi-density of the diffusate to which the lines of flux are normal, and the uniformity of the gradient may be illustrated by drawing any number of lines representing these surfaces of equi-density at equal distances apart.

Although the essential elements of the system have their analogues in the conduction of heat in a bar which has attained the steady state, the parallelism of the two sets of phenomena is only complete if we imagine such a bar to possess no power of thermal emission from its surfaces.

On the other hand, the diffusive flow is strictly analogous to the steady flow of electricity along a conductor of uniform cross-section maintained at its two ends at a constant difference of potential  $V - V_1$ . In this case, the coefficient of diffusivity,  $k$ , corresponds with the electrical conductance, and the surfaces of equi-density with those of equi-potential.

Some time ago Professor Hele Shaw (*Phil. Trans.*, 1901, [4], 95, 303), while investigating the stream lines of a moving viscous film, which is known to obey Fourier's law, discovered that two-dimensional cases of magnetic lines of force can be illustrated in a very beautiful manner by the flow of differently coloured viscous liquids under a constant head of pressure. In a diffusive field, it has not been found practicable up to the present to demonstrate the existence of the actual lines of flux, but, on the other hand, it is quite possible to render visible the surfaces of equi-density of a diffusate, and from these to deduce the shape of the stream lines which are everywhere orthogonal to those surfaces.

In the early days I obtained visual evidence of the shape and

relation of the zones of equi-density in various systems by the intermittent diffusion of solutions of sulphates and chromates into a gel of agar or gelatin to which had been added a little barium chloride. In this way, the surfaces of equal concentration are self-delineated by the progressive bands or zones of the insoluble barium salts precipitated within the gel (see Fig. 1). Latterly for this purpose I have availed myself of the Liesegang phenomena, whereby, under favourable conditions, two opposing diffusive streams of reacting substances can be made to produce in the gel a rhythmical series of zones and bands which follow the contours of surfaces of equi-density.

I have here some examples which show the position of these surfaces as they exist in cylindrical and prismatic diffusion columns.

In hydro-diffusion, most of the coefficients of diffusivity which appear in our tables of physical constants have been derived from the observed rate of flow in columns which have attained the steady condition to which I have referred. The values of  $k$  are generally expressed in centimetre-gram-day units, reference being made to the temperature and the concentration of the solution at the head of the column. Many of the recorded values are only approximations, and have to be treated accordingly. The static method is only rarely applicable to gases, but in a modified form I have shown that it can be successfully employed in determining the diffusivity of atmospheric carbon dioxide in the mixed gases of the air, although its partial pressure is so small.

We have seen that as long as we confine ourselves to the study of diffusive columns which have attained the steady condition of flow, the relations of the various factors which determine the rate of flow and the distribution of density in the column are capable of simple mathematical treatment. If, however, these conditions are not completely fulfilled, and the diffusate is still in process of extension into fresh regions of the column, the particular state of the system can no longer be determined by elementary mathematics, but nevertheless can be deduced from the fundamental equation of Fick when certain definite information is forthcoming as to the conditions of the experiment.

I have here a cylindrical column of agar gel down which is diffusing dilute hydrochloric acid, the concentration of which is maintained constant at the upper face of the column. To this gel has been previously added a little Congo red, and the degree of penetration of the acid is marked by the progressive change of colour from red to blue.

Since the acid diffusate is constantly advancing further and

further from its source, it is evident that any given stratum in the blue part of the column must be receiving more of the acid on its upper surface than it is transmitting from its lower surface to the next similar stratum immediately below it, so that the fall or gradient of density of the diffusate cannot be uniform, as it is in a diffusive column which has attained the static condition. A complete definition of the state of such a system at any desired moment is, however, derivable from the partial differential equation of Fick if we have some means of determining the exact position in the advancing column of a definite and thin stratum where the concentration of the diffusate has a known small value, and we can measure the distance between this stratum and the face of the column, where the acid is maintained at a known concentration.

The extreme limit of the blue coloration corresponds with such a definite stage, and the concentration at this point can be ascertained by a preliminary titration experiment. Knowing the length of the blue column, the ratio of the two concentrations, and the time the experiment has lasted, we have all the elements requisite for calculating the distribution of density in the column and the value of  $k$ .

I am indebted to Sir Joseph Larmor and to Mr. R. A. Fisher for a complete mathematical treatment of this problem, which is practically identical with that of a cooling Earth as investigated many years ago by Lord Kelvin. I need not trouble you with the equation which fits all the required conditions, and will only remark that the calculations are much facilitated by the fact that the equation involves the Probability Integrals of the Normal Curve of Errors, which has been thoroughly tabulated, and is much needed in the Theory of Gases.

One of the conclusions reached during the mathematical analysis is that if a succession of observations are made on such an advancing column of diffusion, the time  $t$  requisite for the extension of the blue coloration along the axis ought to be directly proportional to the square of the length  $x$ , measured from the free surface of the gel, so that  $\frac{x}{\sqrt{t}}$  ought to be constant for all times. How closely this deduction accords with direct experiment will be noticed from the following results, obtained in the diffusion of dilute hydrochloric acid under the described conditions.

Time in hours.	Length of blue column.	$\frac{x}{\sqrt{t}}$ .
$t$ .	$x$ .	
1.0	8.0 mm.	8.00
3.0	14.0 "	8.08
5.5	19.0 "	8.10
7.41	22.0 "	8.08
18.0	34.0 "	8.01
*24.0	40.0 "	8.16

\* By this or some similar method it is quite possible to determine how  $k$ , the coefficient of diffusivity, varies with the initial concentration of the solute at the face of the column.

So far, we have been considering systems in which the stream lines of the diffusive flux are parallel to each other and to the sides of a containing vessel which is cylindrical or prismatic in form. We have seen that in such cases, when the steady condition of flow has been attained, the gradient of density of the diffusate is uniform from end to end of the column, and that this uniformity of gradient can be illustrated by drawing at right angles to the axis, and at equal distances apart, a series of lines corresponding with the surfaces of equi-density. This uniformity of gradient no longer holds good, however, if the stream lines are rendered *convergent* or *divergent* by suitable means.

Suppose, for instance, we have a steady diffusive flow taking place along a tube having the form of a truncated cone. In those regions where the stream lines are more crowded together, that is to say, in the narrower part of the tube, the gradient of density is greater than it is in the wider part. If, therefore, we desire to illustrate this as we have done for the cylinder, we have to draw the lines corresponding with equal decrements or increments of density closer and closer together as the narrower end of the tube is approached.

For a given difference of "diffusion potential" between its two ends, the actual "efficiency" of a conical tube is calculable if we know the length of the truncated cone, its solid angle, and the particular value of  $k$  for the diffusing substance, but as this is only a special case deducible from diffusion around a sphere, which we shall presently consider, I will not dwell on it further except to compare the relative efficiency of a truncated cone and that of a cylindrical tube of the same length which has a uniform cross-section equal to that of the smaller end of the conical tube. This difference may be illustrated by a concrete example.

Suppose we have a truncated cone of 10 cm. in length, the smaller end of which has a spherical area of 1 sq. cm. at a distance of 1 cm. from the apex of the completed cone; then it can be shown that under similar conditions the diffusive flow ought to be *eleven* times greater through the conical tube than through a



cylindrical tube of the same length with a uniform cross-section equal to that of the smaller end of the conical tube.

Such accelerations of the diffusive flow through conical tubes can be readily verified experimentally in various ways. The principle is one which must have an important application in the respiratory organs of air-breathing animals, especially in the alveolar and higher regions of the lungs which lie beyond the influence of the tidal air, and in which the interchange of gases is dependent solely on diffusion.

When a body of spherical shape capable of acting as an absorber or an emitter of a diffusible substance is suspended in a field which is free from convection currents, the direction of the flux, to or from the sphere as the case may be, will be represented by a series of lines drawn radially from its centre, and the surfaces defining regions of equal density of the diffusate will form a series of external shells concentric with the sphere.

Let us first consider a sphere which is acting as an absorber in a practically infinite diffusive field in which the initial concentration has some fixed value represented by  $\rho$ , and that a sufficient time has elapsed to induce the steady condition of flow. We will also assume that the sphere is a perfect absorber, that is to say, that at its immediate surface the concentration of the diffusate is always maintained at zero. Under these conditions, the concentration of the diffusate around the sphere will vary from zero at its immediate surface to a value which is practically  $\rho$  in some region remote from the sphere.

Strictly speaking,  $\rho$  is a limiting value which theoretically is never reached, but for practical purposes it may be regarded as attained at distances exceeding ten diameters of the sphere, so that similar spheres at this distance apart would exercise very little interference with each other.

The distribution of the density or concentration of the diffusate around the sphere will be such that, proceeding from its surface outwards in a radial direction, the defect of density, represented by  $-\rho$ , will vary inversely with the radial distance from the centre of the sphere. Thus at radii 1, 2, 3, 4 . . . the negative densities will be represented by  $-\rho, \frac{\rho}{2}, -\frac{\rho}{3}, -\frac{\rho}{4}, \dots$ , whereas the actual positive densities, measured in the same direction, progress as  $\frac{1}{2}\rho, \frac{2}{3}\rho, \frac{3}{4}\rho \dots$ .

At a distance of, say, 20 radii, the diffusate will consequently have a concentration of  $\frac{19}{20}\rho$ , or within 5 per cent. of the limiting value.

In a system such as this (the steady condition of flow being postulated), it is evident that during any given time interval equal amounts of the diffusate pass through each one of any number of concentric shells of equi-density described around the acting sphere. Since the surfaces of spheres are proportional to the square of their radii, this equality of flow implies that if we compare any two of the shells, the flow through unit area in each case must be inversely proportional to the squares of the radii. The flow per unit area is, however, directly proportional to the gradient of density, so that in such a field of diffusion as we are considering the gradient of density, that is to say, the fall of density per unit of radial length, must everywhere be inversely proportional to the square of the radius.

This leads to the conclusion that if we have two spheres of different dimensions acting as perfect absorbers in the same field of diffusion, and they are placed at such a distance apart as not to interfere with each other sensibly, then their relative *efficiencies*, as defined by the amount of diffusate which they will absorb in a given time, are not proportional to their surfaces, but to their linear dimensions. Thus a sphere of double or half the unit radius will absorb in a given time double or half the amount of diffusate.

If we represent the "efficiency" of an absorbing sphere by  $Q$ , its radius by  $r$ , the maximal concentration of the diffusate at some remote point by  $\rho$ , and the coefficient of diffusivity of the substance by  $k$ , we get the following general expression, which, *mutatis mutandis*, is also applicable to an emitting sphere when the steady condition is reached:

$$Q = 4\pi r\rho k.$$

If the sphere is not a perfect absorber and the diffusate has some ascertainable concentration at its surface, represented by  $\rho_1$ , then we should have to substitute  $\rho - \rho_1$  for  $\rho$  in the above equation.

It will be noted that the phenomena of steady diffusion around a sphere are strictly analogous with those exhibited by a freely suspended and insulated spherical conductor which is electrically charged. The concentric shells of equal density of the diffusate correspond with the shells of equipotential in the dielectric surrounding the charged sphere, whereas the gradient of density measured along the lines of flux corresponds with the gradient of potential around the charged sphere measured along the lines of force. Moreover, what we have termed the 'efficiency' of the diffusive sphere is the exact analogue of the electrostatic *capacity*, both varying directly with the linear dimensions of the sphere.

If in spherical diffusion we describe a series of the concentric

shells of equal density at the appropriate intervals corresponding with equal increments or decrements of density, according to whether the sphere is absorbing or emitting, we obtain a figure which also represents the relative position of the equipotential zones around a charged sphere for equal differences of electrical potential, and in a gravitational field the relative position of the zones corresponding with equal differences of gravitational force.

Further striking and interesting analogies between the electrostatic and diffusive phenomena come to light if we study the lines of force and the equipotential surfaces around two spheres charged to the same electrical potential, and compare these with the surfaces of equi-density and the corresponding lines of diffusive flow induced in a diffusive field by two emitting spheres sufficiently close together to interfere with each other's action.

I will first show you the theoretical disposition of the surfaces of equipotential around two spheres charged to the same potential with electricity of a similar kind.

This illustration (Fig. 2) is taken from a drawing given by Clerk Maxwell in his "Electricity and Magnetism." For the sake of simplicity, I have omitted the actual lines of force, which in this two-dimensional projection would in all cases be normal to the equipotential lines. The forms taken by these lines or surfaces were the result of laborious calculation.

I will now show you (Fig. 3) how in the case of diffusion through two circular apertures the analogous surfaces of equi-density of the diffusate can be self-delineated by the interaction of the stream lines radiating from and to the apertures, thus giving a sectional representation of the shells of equi-density around spheres of corresponding diameters, set at similar distances apart in the same diffusive field. In the particular case shown on the screen, the interfering rings were produced by intermittent diffusion of alkaline sulphates and chromates into a gel containing a little barium chloride. Similar phenomena on a small scale can also be produced by the interference of two sets of Liesegang's rings formed by the diffusion of a solution of lead nitrate through two small apertures in a thin plate of celluloid floated on an agar gel containing a little potassium iodide. Examples of this are before you.

In such a system, however produced, the reacting substances travelling in opposite directions mark out regions of equal concentration of the diffusates, the true stream lines being orthogonal to these surfaces.

It will be noticed, in the first place, that in the early stages of their formation the rings lie closer together around the smaller than around the larger aperture, just as is the case with the zones

FIG. 1.

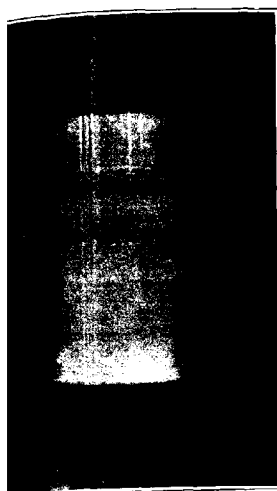


FIG. 2.

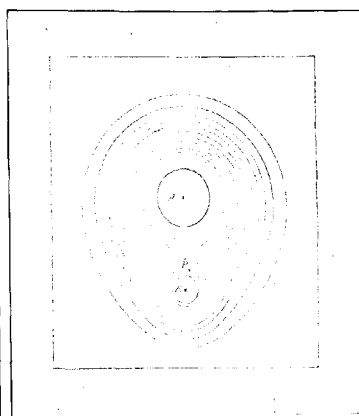
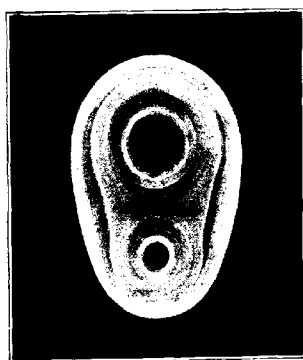


FIG. 3.



(To face page 55)

FIG. 4.

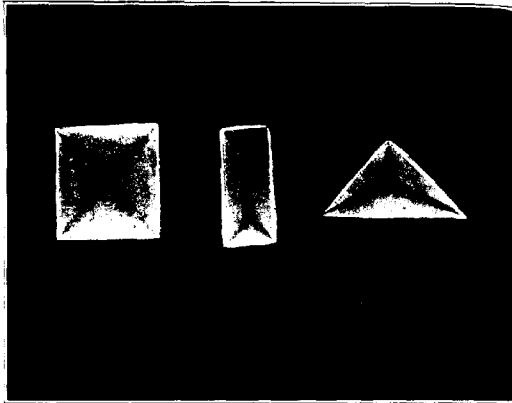


FIG. 5

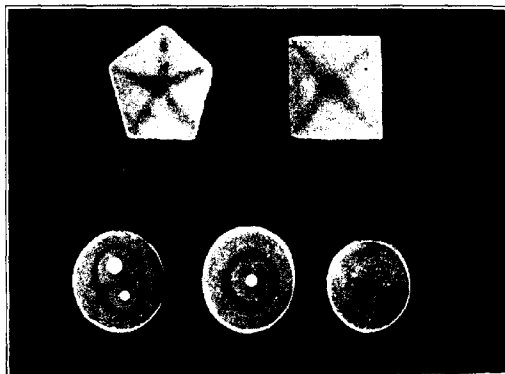


FIG. 6.

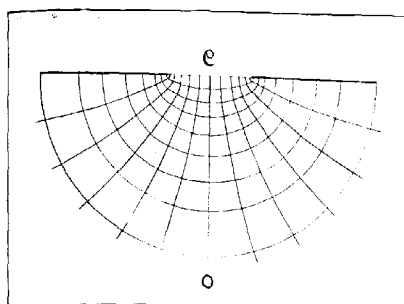


FIG. 7.

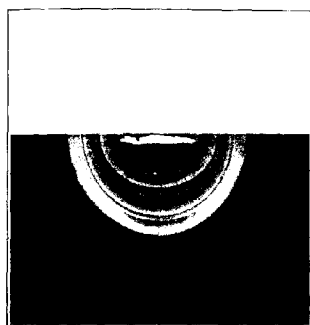
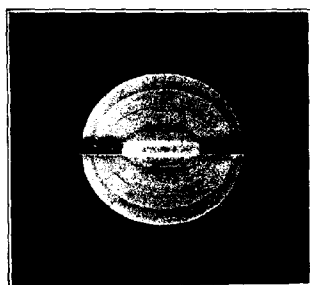


FIG. 8.





## THEIR ANALOGIES AND APPLICATIONS.

of equipotential around two spheres of unequal size electrically charged to the same potential.

As the divergent stream lines of diffusion progress, they begin to interfere with each other, and the rings to which they are normal begin to change their shape, ultimately fusing into a single system similar to the equipotential lines of Clerk Maxwell (see Fig. 2).

The diffusive and the electrostatic systems correspond in every detail. Maxwell by his laborious graphical method showed that any one of the lines of the combined system is regarded as defining the surface of a single body (which in this case would have the shape of a dumb-bell with one end larger than the other), the equipotential surfaces come closer together at the smaller end, further apart at the larger end, where the curvature is less, and furthest apart of all in the centre of the dumb-bell, where the curvature is negative, the relative nearness of the lines indicating the relative density of the charge at these points.

You will see all this well exemplified in the analogous diffusive system. Where the surface curvature is greatest, there the equilibrium lines lie closer together, thus indicating a higher gradient of density in these regions and a greater diffusive flow per unit area.

You will also observe, and perhaps this is the most interesting point of all, that Maxwell marks a certain region ( $P$ , Fig. 2) in the line joining the centres of the electrified spheres, which he states is a point of equilibrium, and that the surface density on a body of the form of this surface would be zero at this point.

This region of equilibrium is also defined in the diffusion figures of Fig. 3 as one of no precipitation; it is, as it were, a "dead spot."

If we fill a tube open at both ends with a gel containing a little barium chloride and then immerse it in dilute sulphuric acid, precipitation of barium sulphate progresses equally from either end of the tube until its centre is approached. There is, however, always a narrow central zone in the middle of the tube which remains clear, no matter what the terminal concentration of the acid may be or how long the experiment has lasted. The same thing occurs when the diffusion of the acid takes place centripetally from the edges of a circular glass cover-glass placed over a drop of the same gel placed on a glass slide, but in this case the dead space takes the form of a circular spot.

The explanation is that the two reacting substances, the sulphuric acid and the barium chloride, are diffusing in opposite directions, and that the barium ions have been depleted from the equilibrium zone before the acid reaches it, a fact which is readily demonstrated



by extruding the column of gel from the tube, dividing it in the centre of the 'dead' region, and applying a little sulphuric acid to the cut ends. When a diffusible coloured substance is employed in solution, the same phenomenon is observed at first, but ultimately, as might be expected, the column shows an equal distribution of colour throughout.

There is a further analogy to certain acoustic phenomena which is not without interest. The dead space in a tube such as I have described corresponds in position with that of the node of an open organ pipe when it is sounding its fundamental note. This analogy may be carried still further. If, for instance, inward diffusion takes place simultaneously from all the four edges of a square cover-glass, the four opposing streams of the reacting diffusates mark out the regions of equilibrium in the form of a regular cross with its arms directed towards the four corners of the square, thus producing an exact picture of the well-known Chladni's figure which marks out the nodes of a square vibrating plate bowed at the centre of one of its edges.

By varying the shape of the plate, a further instructive series of interference diffusion figures can be obtained, of which a few examples are given (see Figs. 4 and 5). On the table are further illustrations of somewhat similar figures produced by Liesegang rings of lead oxide. By suitable arrangement, it is possible to imitate the stratification of natural agates in this manner.

Before leaving the subject of spherical diffusion, I must dwell for a moment on the application of its principles to certain chemical and biological problems.

We have seen that in a diffusive field the actual "efficiency" of a sphere, functioning as an absorber or emitter of the diffusate, varies directly with the radius of the sphere. Hence it follows that if a sphere is divided into any number of spheres  $n$ , of equal volume, and these are distributed in a similar field at such distances apart as not to interfere with each other, then the increased efficiency of the divided system will be represented by  $n\sqrt[3]{\frac{1}{n}}$ , when that of the original sphere is taken as unity. On the other hand, the increase in surface will only be represented by  $\sqrt[3]{n}$ , so that the 'efficiency' increases as the square of the surface.

For instance, if a sphere of unit volume is subdivided into 1000 equal spheres, the surface extension over that of the original sphere

\* The 'efficiency' denotes the rate of emission or absorption for a unit of standard difference of concentration, and is analogous to the electrical capacity of a similar spherical conductor, that is, the charge held for unit difference of potential.

will be represented by 10, whilst the diffusive 'efficiency' of the whole subdivided system will be represented by 100.

The influence of a solid catalyst in increasing the velocity of a chemical reaction, such as that induced by a metal in the 'colloidal' state, is generally attributed to previous adsorption and condensation of the substrate on the surface of the particles.

Let us assume that the particles of the catalyst are spherical, and that the adsorption of the substrate at the boundary of the two phases has to attain a certain small value, which we will call the critical value, before the reaction starts, and, further, that the rate at which the chemical change takes place from this point is practically infinite.

Under these conditions, in order to maintain the rate of change appropriate to the concentration of the substrate in the main body of the liquid, we must retain the concentration at the surface of the particles at its critical value.

If these particles exceed a certain size, this will necessitate more or less vigorous stirring of the liquid. The smaller the particles become, however, the more nearly they will be able to maintain the critical concentration at their surface by diffusion alone, owing to the increasing convergence of the diffusive stream lines producing an ever increasing gradient of concentration. A point will ultimately be reached at which stirring will produce no increased effect.

It has often been assumed that the effect produced by subdivision of the catalyst under these conditions is directly proportional to the area of the surface, but it is evident that under appropriate conditions the activity of a unit mass of a catalyst must vary, not with the surface, but with the *square* of the surface.

These same principles enable us to understand how it is that minute dimensions confer advantages on certain micro-organisms in carrying out their life processes of nutrition and the correlated processes of fermentation and putrefaction.

When these organisms have little or no power of locomotion and the media in which they live have a low degree of mobility, they must be largely dependent on diffusion for the access of material from their surroundings and for the removal of the products of change from their immediate neighbourhood.

Minuteness of dimensions favours these convergent and divergent streams and enables the organism to supply its requirements from a medium of a much lower concentration of substrate than would be the case if the cell were of larger dimensions, thus exemplifying the "importance of being little"—and remaining so (see Slater and Sand, "The Role of Diffusion in Fermentation by Yeast Cells," T., 1910, 97, 922).

Did time allow, I could give further examples of the applications of these same principles to diverse processes in which diffusion plays a more or less prominent part. They are, for instance, operative in the ignition of finely-divided pyrophoric substances, in the sparks produced by flint and steel, and in the rapid propagation of combustion of coal dust and other fine organic substances suspended in air.

We are too apt to regard diffusion as being necessarily a slow process, especially in liquids, which is by no means the case if the gradient of density is enhanced by the extreme convergence of the lines of flux on any particular point.

We have seen how the self-described diffusion figures surrounding two emitting spheres brought into each other's neighbourhood correspond in every detail with Clerk Maxwell's lines of equipotential and lines of force around two similar spheres charged to the same potential with the same kind of electricity.

The diffusion experiment may be so varied as to cause one of the circular perforations, corresponding with the sections of the spheres, to act as an emitter and the other as an absorber or 'sink' of the diffusate.

Under these conditions, the lines of equi-density of the diffusate tend to arrange themselves in accordance with Maxwell's figure of the equipotential lines around spheres, one of which is charged with positive and the other with negative electricity.

It is impossible to regard these analogous phenomena without suspecting that there is also a similarity in the dynamic relations of the two systems. We are, for instance, led to inquire whether in the case of diffusion there are any unbalanced forces which tend to move the bodies in a diffusive field.

I have recently referred this problem, which appears to present great difficulties, to Mr. R. A. Fisher, who is still at work on it. Whatever the final results of his analysis may be, it appears that if a small, elongated body which has a differential power of absorption at its two ends is introduced into a diffusive flow, it will tend to set itself along the lines of flux and to head up stream with its less absorptive end facing the region of the higher concentration of the diffusate.

If this deduction is correct, as I have but little doubt it is, it contains a physical explanation of certain phenomena of chemotaxis which have always been a great puzzle to the biologist. Let me give an example of what I mean.

The fertilisation of the non-motile egg-cells of the ferns and mosses is brought about by free-swimming, highly motile spermatozoids, which crowd into the archegonia in such a manner

as to suggest that there is some emission of an attractive substance from the opening which gives the needed directive force to the spermatozooids.

By immersing the free end of a fine capillary tube charged with a very dilute solution of sucrose into water containing the free-swimming spermatozooids of a moss, Pfeffer was able to demonstrate that whereas the movement of the spermatozooids in the body of the liquid occurred indifferently in all directions, it assumed a uni-directional character in the immediate neighbourhood of the orifice from which the sugar was diffusing, and the organisms crowded into the tube, which acted as a sort of artificial archegonium. Similar chemotactic movements also occur with the spermatozooids of ferns when the capillary is filled with an extremely dilute solution of malic acid. Under certain conditions, the movements are reversed in direction, when the chemotaxis is said to be *negative*. Somewhat similar movements have also been observed in certain motile bacteria, which are "attracted" to regions in which an evolution of oxygen is taking place within the cells of algae containing chlorophyll and suitably illuminated.

Such movements, which at first sight appear to indicate a certain degree of intelligence on the part of the organisms, are, I believe, capable of a very simple physical explanation, which is at any rate worth serious consideration.

It must be borne in mind that in all such cases the real driving force of the spermatozoid or bacterium is supplied by its own motile organs, the flagella; all that we are called upon to explain is the origin of the *directive* force which is exercised when the organism finds itself in a suitable diffusive field in which the gradient of concentration of the diffusing substance is varying in a certain determinate direction.

Such a directive influence will certainly be exerted if the motile organism can act as an *absorber* of the diffusate, and this power of absorption is not uniform over its surface owing to a variation in the degree of permeability of the investing cell-membrane.

If those portions near the 'head' of the spermatozoid are less permeable to the diffusive substance than those nearer the flagellum in the rear, we should expect the organism to orientate itself in such a manner as to head towards the region of higher concentration—that is to say, towards the point of origin of the diffusive flow. This would correspond with the conditions of *positive* chemotactic movement. If, on the other hand, the region of the cell-membrane is more permeable at the front than at the rear, we should expect to get a heading down stream and a consequent re-

cession from the point of origin of the diffusate, that is, *negative* chemotaxis.

We have seen that when two perfectly absorbing spheres of different dimensions are suspended in the same diffusive field at a sufficient distance apart to exert no practical influence on each other, we should expect the ratio of their "efficiencies" as absorbers would be the same as the ratio of their electrostatic capacities when once the steady condition of diffusion has been induced. This should be equally true of bodies of any shape, so that if by experimental or other means both the electric capacity and volume of the body are known, we can by analogy determine its diffusive efficiency in a given field by referring it to that of a sphere of equal volume.

In the case of freely suspended spheres, the experimental verification of this proposition presents certain difficulties, which can, however, be avoided by a further simplification of the problem, as follows:

Clerk Maxwell has shown how it is possible to calculate the electric capacity of a planetary or oblate spheroid, which is formed by the revolution of an ellipse around its minor or polar axis, and to refer this capacity to that of a sphere of unit radius. Now a circular disk may be regarded as a particular and extreme case of a planetary ellipsoid in which the minor or polar axis has vanished. Such a disk if embedded flush in a non-conducting material has an electrostatic capacity of  $\frac{1}{2\pi}$  times that of a sphere of the same radius. Hence, if the analogy really holds good, we should expect the "diffusive efficiency" of a disk to be represented by

$$\frac{4\pi krp}{\frac{1}{2\pi}} = 8krp,$$

if we count both sides of the disk, or  $4krp$  if the disk is absorbing or emitting on one side only.

We may substitute for such a disk a circular aperture in a very thin diaphragm through which diffusion is allowed to go on under well-defined conditions.

In these circumstances, by measuring the rate of flow of atmospheric carbon dioxide or of water vapour through circular apertures of known dimensions into a suitable vessel which ensures its absorption on the other side of the diaphragm, I have been able to obtain very complete evidence that experience and theory are in accord. Moreover, it is easy also to demonstrate that the rate of diffusive flow is directly proportional to the linear dimensions of

the aperture, not to its area. In fact, all the observed phenomena in their quantitative relations are strictly in accordance with those deducible from the application of the electrostatic analogy.

By using a method of this kind, it is quite possible in some cases to determine with considerable exactness coefficients of diffusivity, and it was in this manner that I was enabled to determine the value of  $k$ , the coefficient of interdiffusion of carbon dioxide and air, for dilutions of carbon dioxide representing about  $3/10,000$  of an atmosphere.

The conditions of evaporation in still air from a circular surface of liquid surrounded by a wide rim were mathematically investigated by Stefan in 1881, who also made use of the electrostatic analogy.

He concluded that the rate of evaporation in perfectly still air ought to be proportional to the linear dimensions of the liquid surface, and not, as was commonly supposed, to its area. Further, his analysis indicated that the divergent lines of flux of vapour emitted from the surface ought to be represented by a series of hyperbolas having their common foci in the bounding edge of the circular surface, whilst the curved surfaces of equal partial pressure of the vapour overlying the disk should form an orthogonal system of ellipsoids, also having their foci in the edge of the disk. Since these ellipsoids, conforming to surfaces of equal partial pressure, necessarily come closer together at the margin of the disk than towards its centre, Stefan concluded that, under the conditions postulated, evaporation proceeds more rapidly at the edge than at the centre.

Such a system is illustrated in a reversed position in Fig. 6, which also represents equally well the distribution of the lines of force and surfaces of equipotential in the neighbourhood of a circular electrified disk embedded flush in a wide, non-conducting rim.

I am not aware that Stefan or his successors ever attempted to verify his deductions by actual experiment. I am able this evening to show you how this can be done.

In the first attempts made by my colleague, Mr. F. Escombe, and myself, we used a rectangular glass cell divided horizontally by a plate of celluloid having a circular hole punched through it. The lower half of the cell was completely filled with a gelatin gel containing a little barium chloride, and the upper half with a solution of alkaline sulphate. The opposing streams of the reacting diffusates produced in the gel in the neighbourhood of the aperture an opaque spheroidal figure which changed its shape as it became larger. By photographing this at intervals and super-

imposing the negatives, it was seen that the limiting surfaces of the constantly changing figure marked out by the precipitation of the barium sulphate conformed exactly to the system of ellipsoids demanded by theory.

The process was further improved by the intermittent diffusion of sulphates and chromates through the aperture, thus forming a banded structure in the gel, well seen when the block of gelatin was divided by a vertical section. This further led to employing a semicircular aperture with its flat side coincident with the plane of one of the sides of the glass vessel, so that the arrangement of the banded structure on the diffusion spheroids was visible in cross-section through the glass. Further developments led to the use of narrow slits cut in a thin plate of celluloid which formed one side of a thin, rectangular cell filled with the gelatin-barium mixture. Such a slit manifestly corresponds with a vertical central section of a circular disk looked at edgewise.

In the slides now before you (Figs. 7 and 8) you have a photographic reproduction of such a system of the shells of equi-density in the immediate neighbourhood of the opening through which the diffusion is taking place. It will be noted that their shape and disposition are exactly those predicted by Stefan, the alternate zones of barium sulphate and chromate forming a series of confoal ellipsoids having their foci in the edges of the disk, and therefore approximating more and more to the spherical shape as we progress outwards. It is also to be observed that the ellipsoidal shells come closer together at the edges than in the centre, indicating that in these regions the gradient of density is greater, and consequently that the flow per unit area is also greater.

It must not, however, be supposed, as I have sometimes seen it stated, that the acceleration of diffusive flow produced by small apertures is dependent merely on this increased flow at the edges. There would be almost the same amount of acceleration if the equi-density zones could be imagined to be spherical instead of ellipsoidal. The acceleration of flow per unit area as the size of the aperture is diminished is conditioned in the main by the degree of convergence or of divergence of the lines of flux. The smaller the aperture, the greater becomes this convergence and divergence, with a corresponding increase in the gradient of density in its immediate neighbourhood.

The experimental study of diffusion through single apertures naturally leads up to a consideration of the effects to be expected from a series of small apertures in a thin diaphragm when such a multi-perforate septum is inserted in a line of diffusive flow.

One would expect, from what has been said, that if the apertures are small and arranged at suitable distances apart, the accelerated flow induced by each individual aperture would to a large extent neutralise the effect of the obstruction produced by the imperforate parts of the diaphragm, and that under favourable conditions the intervention of such a septum would not sensibly diminish the rate of flow in the diffusive column, although the aggregate area of the openings might be small as compared with the cross-section of the column.

This was actually found to be the case. As an instance, I may mention an experiment in which a thin film of celluloid perforated with 100 circular apertures per sq. cm., each one of a radius of 0.19 mm., produced no sensible effect in obstructing the static diffusion of atmospheric carbon dioxide down a column of air, although the imperforate parts of the septum blocked out nearly 90 per cent. of the cross-section of the column.

Just as the electric capacity of a plate is not considerably affected by cutting parts of it away and leaving an open framework, so also it is possible to block out a considerable portion of the cross-section of a diffusive column without materially altering the general static conditions on which the flow depends. In such a case, what I have termed the *diffusive efficiency* of the system is but little affected.

I have here a demonstration of this principle in these two columns of gel into which a dye has been diffusing for some time. In one case the column is entirely unobstructed, whereas in the other such a perforated septum as I have described has been inserted in the line of flow, thus cutting off about 90 per cent. of its effective area. You will notice that the efficiency of the column has not been sensibly reduced in the latter case.

In the accompanying illustration (Fig. 9), I have attempted to illustrate in diagrammatic form the manner in which the parallel lines of flux in a diffusive column are modified by the interposition of such a perforated septum. It will be noted that as the streamlines approach the apertures they become convergent and gradually resume parallelism again on the other side, since the lines of flux, the lines of force, cannot intersect each other.

On the other hand, there is an increased gradient of density in the immediate neighbourhood of the apertures, as evidenced by the lines of equi-density coming closer together in this region, and producing a more rapid flow through the septum.

That such a theoretical system conforms to the actual facts is shown by the succeeding illustration (Fig. 10), which shows a photograph of the zones of equi-density under these conditions produced



by intermittent diffusion of two reacting substances through a series of apertures.

In this principle resides the long-sought explanation of the effectiveness of the stomata of a green leaf in accelerating the interchanges of gases and water vapour which are requisite for the requirements of the plant.

From the dimensions and mode of distribution of these stomata, it is quite possible to calculate what their maximum diffusive efficiency ought to be under given conditions, both for carbon dioxide and water vapour, and to compare this with the actual interchanges as determined by experiment.

In all such cases as have been examined the theoretical efficiency of the mechanism, regarded merely as a piece of physical apparatus, is far in excess of any demands which could be made upon it. Whatever limiting factors may exist in the co-ordinated processes attendant on carbohydrate assimilation by a green leaf, whether of a physical or chemical nature, we cannot attribute any of them to faulty construction in the diffusive mechanism itself.

It is certainly extremely improbable that the green leaf is the only case in nature in which there has been a more or less perfect adaptation to these laws of diffusion through small apertures. It is true that up to the present it is the only instance in which a complete and satisfactory demonstration has been forthcoming of this remarkable adjustment of structure to function, but doubtless there exist many other examples of equal interest and importance which await further discovery. It is impossible, for instance, to observe the minute perforations in the closing membranes of certain vegetable cells without recognising how eminently suited these structures are for producing all the diffusive phenomena which belong to multi-perforate septa, and how admirably they are adapted, without any sacrifice of protective strength, to enhancing the rate of diffusive flow through the cell membrane separating contiguous cells.

Nor are these suggestive facts by any means confined to the Vegetable Kingdom.

It is many years ago since Graham hazarded the opinion that when insects are at rest and exerting no muscular effort of any kind, their respiratory processes are carried on entirely by diffusion along the ramifying tracheæ which communicate with the outer air through the stigmatic openings in the body segments.

The accuracy of this guess is rendered still more probable when we examine the structure of these stigmatic openings more closely.

I am indebted to Mrs. Cuthbert Baines for a beautiful microscopical drawing of the stigma of a caterpillar in medial cross-

section, from which you will see that the apparatus has in certain respects such a remarkable resemblance to the stoma of a leaf that it is impossible to avoid the conclusion that the gaseous exchanges of respiration in the insect are in a measure determined by this particular structure (see Fig. 11).

To elaborate and give the necessary proof of many of the statements I have made this evening would require, not one, but many lectures. The present summary, imperfect and discursive as it may appear, may nevertheless suffice to show that much may be expected from a continued study of diffusion and the application of its principles in various branches of science. One of the greatest pleasures of which the human mind is capable is engendered by this linking together of diverse sets of phenomena by some underlying common principle which is not at first recognisable. How well was this expressed nearly two thousand years ago by one who was both a great poet and a keen observer of nature: one who found his best solace and inspiration in the study of his forests, his flocks and herds, his vineyards, his corn lands and his hives!

“Felix qui potuit rerum cognoscere causas.”

## XLVI.—Some Piperylhydrazones.

By ALBERT WEINHAGEN.

The piperylhydrazine employed in this investigation was prepared by reducing nitrosopiperidine (Knorr, *Annalen*, 1883, **221**, 304). Unless otherwise stated, the condensations were effected according to the usual method of heating the aldehydes with the requisite amount of piperylhydrazine in alcoholic solution faintly acidified with acetic acid. As described in each instance, the products were then purified by such methods as proved most suitable.

*Piperonalpiperylhydrazone*.—This crystallises from alcohol in colourless needles melting at 65–67°. The hydrazone is readily soluble in ether, chloroform, benzene, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0.1916 gave 21.1 c.c.  $N_2$  at 17° and 722 mm.  $N=12.31$ .

$C_{13}H_{16}O_2N_2$  requires  $N=12.07$  per cent.

*Salicylaldehydepiperylhydrazone*.—This compound crystallises from alcohol in needles, at times in small rhombic plates, and

occasionally in octahedra, which interlace in such a manner as to form long, needle-like, prismatic structures. The compound melts at  $71-72^{\circ}$ , and is readily soluble in ether, chloroform, benzene, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0.1965 gave 24.7 c.c.  $N_2$  at  $17^{\circ}$  and 711 mm.  $N=13.84$ .

$C_{12}H_{16}ON_2$  requires  $N=13.74$  per cent.

*Formaldehydepiperylhydrazone*.—This crystallises from alcohol in prismatic needles melting at  $78-79^{\circ}$ . It is readily soluble in chloroform, hot light petroleum, or hot alcohol, less readily so in cold light petroleum or cold alcohol, and practically insoluble in water:

0.1270 gave 28.3 c.c.  $N_2$  at  $16^{\circ}$  and 728 mm.  $N=25.21$ .

$C_6H_{12}N_2$  requires  $N=25.21$  per cent.

*Benzaldehydepiperylhydrazone*.—This hydrazone crystallises from alcohol in small, five- or six-sided plates. The pure compound (which was analysed) melted at  $68-69^{\circ}$  (Knorr, *loc. cit.*, gives  $62-63^{\circ}$ , and Forster, T., 1915, 107, 267, gives  $68^{\circ}$ ).

*Anisaldehydepiperylhydrazone*.—Three grams of anisaldehyde were heated on the water-bath with 2 grams of piperylhydrazine and 2 grams of 50 per cent. acetic acid. The mixture soon became red, and ultimately an intensely reddish-violet syrup separated, which became crystalline on evaporating to dryness and allowing to remain for some time. By means of light petroleum, the hydrazone can be extracted from this mixture free from the red colouring matter, for the latter, whilst being readily soluble in alcohol, is quite insoluble in the former solvent. On evaporating the light petroleum, the hydrazone was obtained in small, colourless, hexagonal plates. The hydrazone obtained in this way possessed the property of turning reddish-violet when exposed to light, which was evidently due to traces of impurities. This ceased to be the case after it had been recrystallised from alcohol several times. The melting point ultimately remained constant at  $54^{\circ}$ . The hydrazone is readily soluble in ether, chloroform, light petroleum, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0.1897 gave 21.8 c.c.  $N_2$  at  $16^{\circ}$  and 728 mm.  $N=12.79$ .

$C_{13}H_{18}ON_2$  requires  $N=12.85$  per cent.

An attempt was made to avoid the formation of the reddish-violet colouring matter by condensing in alcoholic solution, but the results were precisely the same as before.

*p-Hydroxybenzaldehydepiperylhydrazone*. — This compound

separated from an alcoholic solution of 3 grams of piperylhydrazine, 4.5 grams of *p*-hydroxybenzaldehyde, and acetic acid, which had remained at the ordinary temperature for several days, whereas if the mixture is heated, a much inferior yield, accompanied by resinous red by-products, is obtained. The hydrazone is soluble in ether, chloroform, or hot alcohol. When recrystallised from the latter solvent, it melts at 161°:

0.1799 gave 22.7 c.c.  $N_2$  at 18° and 726 mm.  $N=13.91$ .

$C_{12}H_{16}ON_2$  requires  $N=13.74$  per cent.

*p*-Aminoacetophenonepiperylhydrazone.—Three grams of *p*-aminoacetophenone dissolved in alcohol were heated on the water-bath with 2 grams of piperylhydrazine and 2 grams of 50 per cent. acetic acid. The solution soon became yellow, and on cooling the mixture and allowing it to remain, no hydrazone separated. The mixture was accordingly evaporated to dryness. The brown, syrupy substance obtained in this way was practically insoluble in light petroleum, but treatment with this solvent converted it into a granular, faintly yellow mass, which was recrystallised from 95 per cent. alcohol several times. The pure white hydrazone obtained in this way crystallises in small prisms and prismatic needles melting at 108°. It is readily soluble in ether or hot alcohol, less readily so in cold alcohol, very sparingly so in light petroleum, and practically insoluble in water:

0.1468 gave 0.0110  $H_2O$  at 110°.  $H_2O=7.49$ .

0.1889 „ 30.4 c.c.  $N_2$  at 16° and 728 mm.  $N=17.90$ .

$C_{13}H_{19}N_3.H_2O$  requires  $H_2O=7.66$ ;  $N=17.89$  per cent.

Hot dilute hydrochloric acid readily resolves this hydrazone into its components, of which *p*-aminoacetophenone was isolated and recognised by means of its platinichloride (Found:  $Pt=28.78$ . Calc.:  $Pt=28.69$  per cent.).

Attempts to prepare the piperylhydrazones of propionaldehyde, acetone, *p*-aminobenzaldehyde, dextrose, galactose, and *l*-xylose gave rise to resinous red and brown products, whereas isovaleraldehyde furnished very small yields of a compound melting at approximately 122°, which was not analysed.

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# XLVII.—*Acetyl-p-diazoimides derived from Substituted p-Phenylenediamines.*

By GILBERT T. MORGAN and DAVID ALEXANDER CLEAGE.

RECENT experiments on the diazotisation of acyl-*p*-phenylenediamines carried out with nitrous anhydride in dry solvents have led to the isolation of the simpler acyl-*p*-phenylenediazoimides containing respectively formyl, acetyl, and benzoyl groups (Upton and Morgan, T., 1917, 111, 187). These results have since been confirmed by Dimroth and Leichtlin (*Ber.*, 1917, 50, 1539), who have prepared benzoyl-*p*-phenylenediazoimide in aqueous solutions by the action of sodium hydroxide on benzoylaminonaphthalene-4-diazonium chloride.

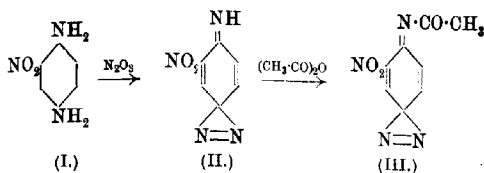
Researches extending over many years have shown that the formation of acyl-*p*-diazoimides from aromatic acyl-*p*-diamines is a general reaction which has been realised in a very large number of instances (T., 1905, 87, 73, 921, 1302; 1906, 89, 4, 1158, 1289; 1907, 91, 1505, 1512; 1908, 93, 602, 614; 1910, 97, 48; *Ber.*, 1902, 35, 888; 1906, 39, 2869).

These results indicate that the presence of the acyl group doubtless plays an important part in the internal condensation leading to the production of acyl-*p*-diazoimides, yet there is a possibility that under suitable experimental conditions it might be possible to isolate the parent substances of this series of diazo-derivatives in which the acyl radicle is replaced by hydrogen.

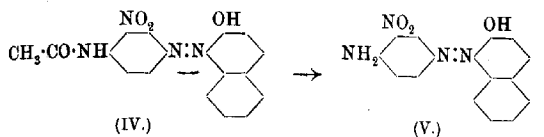
With this object in view, the experiments recorded in the experimental section have been made on derivatives of *p*-phenylenediamine containing acidic substituents in the nucleus.

The difficulty of diazotising both amino-groups simultaneously in *p*-phenylenediamine is greatly increased when a nitro-group is introduced into the ring. Nitro-*p*-phenylenediamine (I) is accordingly a suitable base for the attempt to isolate a diazoimine produced by the diazotisation of only one of the amino-groups.

When this experiment is carried out with nitrous anhydride in well-cooled anhydrous solvents, an unstable, brown substance having the properties of a diazoimine (II) is produced. This product, however, becomes resinous when warmed to the ordinary temperature; it is stable only in a freezing mixture. While suspended in a cooled mixture of ether and acetone, this diazoimine can, however, be stabilised by acetylation with acetic anhydride, when 4-acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide (III) is obtained:

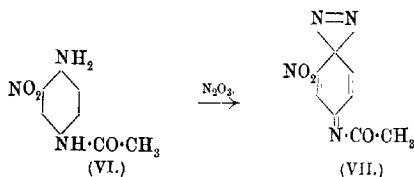


The constitution of this acetyl derivative, and hence that of the unstable diazoimide, are confirmed by the following series of reactions. The acyl-*p*-diazoimide is combined with  $\beta$ -naphthol to form the azo-derivative (IV), and this compound is hydrolysed to the

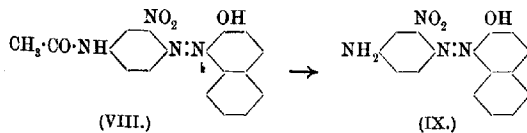


corresponding aminoazo-derivative (V). The latter product when diazotised and boiled with alcohol is converted into *m*-nitrobenzene-azo- $\beta$ -naphthol, which is identified by direct comparison with the preparation obtained by combining diazotised *m*-nitroaniline and  $\beta$ -naphthol.

Further confirmation of this constitution for 4-acetyl-3-nitro-phenylene-1-diazo-4-imide is obtained by preparing its isomeride, 4-acetyl-2-nitro-*p*-phenylene-1-diazo-4-imide (VII). This diazo-imide, obtained in a similar manner by diazotising 4-acetyl-2-nitro-*p*-phenylenediamine (VI) with nitrous anhydride in dry acetone,



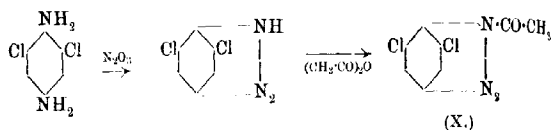
combines with  $\beta$ -naphthol to yield an azo-derivative (VIII), which on hydrolysis gives rise to an aminoazo-compound (IX). From



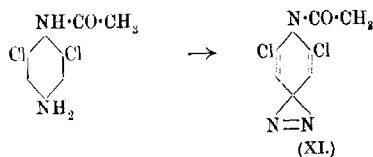
this aminoazo-derivative, elimination of the amino-group through the diazo-reaction leads to *o*-nitrobenzeneazo- $\beta$ -naphthol, which can be compared directly with the product obtained by combining *o*-nitrobenzenediazonium chloride and  $\beta$ -naphthol.

These results demonstrate the constitution of the two isomeric acetyl-*p*-diazoidimides (III and VII) derived from 2-nitro-4-phenylenediamine, the former of which is obtained by acetylating the diazoimine of this diamine.

Similar results have been obtained in the case of 2:6-dichloro-4-phenylenediamine. This base on treatment with nitrous anhydride in well-cooled acetone yields an unstable diazoimine which can be stabilised by acetylation:



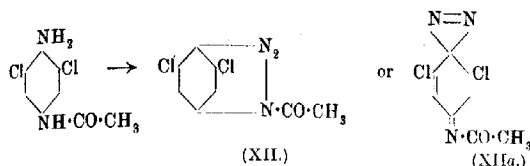
The product (X), a grey, crystalline powder, combined readily with the naphthols and naphthylamines, giving colour reactions identical with those obtained from the diazoimide (XI) prepared by diazotising 1-acetyl-2:6-dichloro-*p*-phenylenediamine:



The latter diazoimide has, however, a bright yellow colour. The colour differences may possibly be due to the first compound being the cyclic diazoimide (X), whilst the latter is the diazoquinonimide (XI). Or, alternatively, the less coloured compound might be a diazonium derivative and the other a diazo-compound. These differences, however, disappear on combining with phenols or reactive bases both forms of acetyl-3:5-dichloro-*p*-phenylene-1-diazo-4-imide giving the same azo-derivatives.

The alternative formulations (XII or XIIa) for the product of acetylation of 2:6-dichloro-*p*-phenylenediamine is excluded by direct experimental evidence.

Acetyl-2:6-dichloro-*p*-phenylene-1-diazo-4-imide (XII) is prepared by treating 4-acetyl-2:6-dichloro-*p*-phenylenediamine with nitrous anhydride under similar conditions:



The product, which is stable at the ordinary temperature, is almost colourless, thus suggesting the diazoimide configuration (XII) rather than that of the diazoquinoneimide (XIIa). It combines readily with the naphthols and naphthylamines, giving colour indications differing from those of the two forms of acetyl-3:5-dichloro-*p*-phenylene-1-diazo-4-imide.

# EXPERIMENTAL.

## 4-Acetyl-2-nitro-*p*-phenylene-1-diazo-4-imide (VII).

*p*-Phenylenediamine was acetylated by adding acetic anhydride (1·3 parts) to its 40 per cent. aqueous solution. The diacetyl derivative when nitrated either in glacial acetic acid or in concentrated sulphuric acid (compare *Ber.*, 1897, **30**, 980) gave its own weight of diacetyl-2-nitro-*p*-phenylenediamine. This product was half hydrolysed to 4-acetyl-2-nitro-*p*-phenylenediamine by boiling for fifteen minutes with 2 parts of crystallised barium hydroxide and 3 parts of water, the barium being then removed by passing carbon dioxide into the boiling solution. The filtrate on cooling deposited bulky, orange-red plates melting at 188°.

4-Acetyl-2-nitro-*p*-phenylenediamine (1 part) dissolved in 100 parts of pure dehydrated acetone was treated slowly with 5 c.c. of a 10 per cent. acetone solution of nitrous anhydride free from nitrogen peroxide, both solutions being cooled to -15°. The colour of the solution of the base changed from red to pale straw-yellow, and on the addition of an equal volume of pure dry ether the product separated in yellow plates, and was washed with anhydrous ether and dried in a vacuum desiccator in the dark:

0·1000 gave 22·5 c.c. N<sub>2</sub> (moist) at 9° and 770·8 mm. N = 27·31.

C<sub>8</sub>H<sub>6</sub>O<sub>3</sub>N<sub>4</sub> requires N = 27·18 per cent.

4-Acetyl-2-nitro-*p*-phenylene-1-diazo-4-imide decomposed explosively at 142°. It darkened on exposure to light, and combined readily with *β*-naphthol when the two reagents were ground together.



*Constitution of Acetyl-2-nitro-p-phenylene-1-diazo-4-imide.*

Acetyl-2-nitrophenylene-1-diazo-4-imide was combined with  $\beta$ -naphthol (1 mol.) in glacial acetic acid. The product, a red azo- $\beta$ -naphthol, melted at  $298^{\circ}$ , and developed a magenta coloration with concentrated sulphuric acid. When the saturated solution of this azo-derivative in glacial acetic acid was diluted with three volumes of water and warmed with excess of concentrated ammonia, the acetyl group was removed by hydrolysis. The resulting 2-nitro-4-aminobenzeneazo- $\beta$ -naphthol was dissolved in absolute alcohol and treated with nitrous anhydride and a few drops of concentrated sulphuric acid at  $-10^{\circ}$  to  $-15^{\circ}$ . This diazonium solution combined with alkaline  $\beta$ -naphthol to a dark red bisazo-compound, giving an orange coloration with concentrated sulphuric acid. Another portion of the alcoholic diazonium solution was boiled gently, when nitrogen was evolved. The dark red powder left on evaporating the alcoholic solution was crystallised from 80 per cent. alcohol containing animal charcoal. It then melted at  $206^{\circ}$  and gave a reddish-violet coloration with concentrated sulphuric acid. A specimen of 2-nitrobenzeneazo- $\beta$ -naphthol was prepared for comparison from  $\beta$ -naphthol and diazotised *o*-nitro-aniline; it was a brownish-red to dark red powder melting at  $209^{\circ}$  and giving a violet coloration with concentrated sulphuric acid. The melting point of a mixture of the two preparations varied from  $203^{\circ}$  to  $205^{\circ}$ . In this way, the orientation of the nitro-group with respect to the diazo-group was ascertained and the constitution of the acetyl-diazoimide determined. 4-Acetyl-2-nitro-p-phenylene-1-diazo-4-imide gave the following colour reactions on conversion into its azo-derivatives; this combination being effected in pyridine:

Azo-derivative with:	Colour of the azo-derivatives.	Coloration with concentrated sulphuric acid.
$\beta$ -Naphthol .....	Scarlet	Magenta
$\beta$ -Naphthylamine .....	Red	Brownish-red
$\alpha$ -Naphthol .....	Scarlet	Emerald green
$\alpha$ -Naphthylamine .....	Crimson	Purple

*3-Nitro-p-phenylene-1-diazo-4-imine and its Acetyl Derivative.*

2-Nitro-*p*-phenylenediamine in dry acetone solution yielded on treatment with nitrous anhydride dissolved in the same solvent a diazo-derivative which separated as a brown, crystalline precipitate on adding dry ether at  $-15^{\circ}$ . On attaining the ordinary temperature, this product resinified and lost its power of combining with  $\beta$ -naphthol to form an azo-derivative.

The acetyl derivative of this unstable diazo-compound was isolated by the following procedure. 4-Acetyl-2-nitro-*p*-phenylenediamine (1 gram) dissolved in 100 c.c. of dry acetone was treated successively with 10 c.c. of a 10 per cent. acetone solution of nitrous anhydride and 0.40 c.c. of acetic anhydride. The colour of the solution of the base changed from crimson to brown. The addition of 80 c.c. of ether produced a precipitate, probably consisting of unacetylated diazoimine, which dissolved again as acetylation proceeded, the acetyl derivative separating on the addition of a further 100 c.c. of ether in brownish-red plates exploding violently at 140°:

0.1500 gave 35.3 c.c.  $N_2$  at 18° and 773.6 mm.\*  $N = 27.70$ .

$C_8H_6O_3N_4$  requires  $N = 27.18$  per cent.

*Constitution of 4-Acetyl-3-nitro-p-phenylene-1-diazo-4-imide.*

The azo- $\beta$ -naphthol compound of 4-acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide was a dark red powder melting above 290°. Its saturated solution in glacial acetic acid was diluted with three volumes of water and the liquid rendered alkaline with concentrated aqueous ammonia. This treatment led to hydrolysis of the acetyl group in the azo-derivative. The resulting 3-nitro-4-aminobenzenazo- $\beta$ -naphthol, a pale brown powder melting at 208°, and developing a claret coloration with concentrated sulphuric acid, was diazotised by adding nitrous acid at -10° to -15° to its solution in absolute alcohol. The diazo-compound gave with alkaline  $\beta$ -naphthol a brown bisazo-derivative, developing a yellow coloration with concentrated sulphuric acid.

On warming an alcoholic solution of the diazo-compound of -nitro-4-aminobenzenazo- $\beta$ -naphthol, nitrogen was evolved, and the liquid on evaporation left a dark, tarry mass from which -nitrobenzenazo- $\beta$ -naphthol was extracted on boiling with 80 per cent. alcohol and animal charcoal. The filtrate on cooling deposited bright yellowish-orange crystals which melted at 192°, and developed a bright cherry-red coloration with concentrated sulphuric acid. For the purpose of comparison, *m*-nitroaniline was converted successively into 3-nitrobenzenediazonium chloride and 3-nitrobenzenazo- $\beta$ -naphthol. The latter compound melted at 194° and gave a similar cherry-red coloration with concentrated sulphuric acid. The melting point of a mixture of the two preparations varied between 189° and 192°.

4-Acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide gave the following

\* In this and the following estimations the nitrogen was measured over 1 per cent. potassium hydroxide

colour reactions when converted into its azo-derivatives by combining in the presence of pyridine:

Azo-compound with:	Colour of azo-compound.	Coloration with concentrated sulphuric acid.
$\beta$ -Naphthol .....	Brownish-red	Magenta red
$\beta$ -Naphthylamine .....	Brownish-red	Brown
$\alpha$ -Naphthol .....	Reddish-brown	Olive green
$\alpha$ -Naphthylamine .....	Dark red	Magenta red

*Acetyl-p-diazoimides derived from 2:6-Dichloro-p-phenylene-diamine.*

A solution of 1 part of *p*-nitroaniline in 3 parts of glacial acetic acid and 6 parts of concentrated hydrochloric acid was cooled to 0° and treated with chlorine until 2 molecular proportions of the gas had been used. The mixture was kept thoroughly stirred throughout the chlorination, and the lemon-yellow precipitate of 2:6-dichloro-4-nitroaniline was obtained in theoretical yield (compare Flürscheim, T., 1908, **93**, 1773). This nitro-compound (1 part) and ammonium chloride ( $\frac{3}{8}$  part) were dissolved in 25 parts of 50 per cent. alcohol, and 1 part of zinc dust (80 per cent. Zn) was added slowly to the boiling solution. The mixture was heated under reflux for half an hour until the colour changed from yellow to light grey. The filtrate from the precipitate of zinc and zinc hydroxide was then distilled and the greater part of the alcohol thus recovered. 2:6-Dichloro-4-phenylenediamine separated from the residual solution in colourless plates, becoming brown with a bronzy reflex on exposure to the air. The yield was 90 per cent. of the calculated quantity.

*4-Acetyl-2:6-dichloro-p-phenylene-1-diazo-4-imide.*

2:6-Dichloro-*p*-phenylenediamine (1 part) dissolved in 50 parts of warm water was acetylated by the addition of 1 part of acetic anhydride. The solution, which was vigorously stirred during the reaction, became speedily filled with colourless crystals of 4-acetyl-2:6-dichloro-*p*-phenylenediamine. The crude product was then recrystallised from hot water, from which it separated in colourless needles melting at 200°. One part of this acetyl compound dissolved in 100 parts of dry acetone and cooled to -15° was diazotised with 8.5 parts of a 10 per cent. solution of nitrous anhydride in the same solvent. On adding 100 parts of dry ether, the diazo-imide separated as a pale yellowish-white, microcrystalline precipitate:

0.1500 gave 23.2 c.c. N<sub>2</sub> at 18.5° and 773 mm. N=18.27.

C<sub>8</sub>H<sub>5</sub>ON<sub>3</sub>Cl<sub>2</sub> requires N=18.25 per cent.

4-Acetyl-2:6-dichloro-*p*-phenylene-1-diazo-4-imide was obtained in almost colourless plates decomposing explosively at 138°. This diazoimide coupled additively with the following developers either in the dry state or when mixed with pyridine:

Developer.	Colour of Azo-compound.	Coloration with concentrated sulphuric acid.
$\beta$ -Naphthol .....	Orange-red	Bluish-red
$\beta$ -Naphthylamine .....	Brownish-red	Brown
$\alpha$ -Naphthol .....	Brownish-red	Green
$\alpha$ -Naphthylamine .....	Red	Reddish-brown
Chromotropic acid .....	Cerise	Olive green

1-Acetyl-3:5-dichloro-*p*-phenylene-1-diazo-4-imide.

(1) *Preparation from 1-Acetyl-2:6-dichloro-*p*-phenylenediamine.*—2:6-Dichloro-4-phenylenediamine (10 grams) was heated for one hour in a reflux apparatus with 10 c.c. of acetyl chloride, when diacetyl-2:6-dichloro-*p*-phenylenediamine separated on cooling. The crude product when crystallised from hot water melted at 254°. 1-Acetyl-2:6-dichloro-*p*-phenylenediamine was prepared by half hydrolysing the diacetyl compound. The latter was boiled for fifteen minutes with 30 parts of *N*-sodium hydroxide solution, when, on cooling, the monoacetyl derivative separated in lustrous, colourless plates which, after recrystallisation from water, melted at 218°. Three parts of 1-acetyl-2:6-dichloro-*p*-phenylenediamine dissolved in 120 parts of dry acetone were diazotised with 1 part of nitrous anhydride dissolved in 10 parts of the same solvent. During diazotisation, the solution was thoroughly stirred, when the colour changed to bright yellow; the precipitation of yellow diazoimide then commenced, and was completed by the addition of 60 parts of dry ether:

0.2050 gave 32.5 c.c.  $N_2$  at 18° and 762 mm.  $N = 18.37$ .

$C_8H_5ON_3Cl_2$  requires  $N = 18.25$  per cent.

1-Acetyl-3:5-dichloro-*p*-phenylene-1-diazo-4-imide is an orange-yellow, crystalline powder, very sensitive to light, changing rapidly to chocolate, and decomposing at 133°. It combined additively with the following developers on mixing either in the dry state or in pyridine:

Developer.	Colour of azo-compound.	Coloration with concentrated sulphuric acid.
$\beta$ -Naphthol .....	Orange-red	Scarlet
$\beta$ -Naphthylamine .....	Orange	Blue
$\alpha$ -Naphthol .....	Brownish-red	Green
$\alpha$ -Naphthylamine .....	Orange	Scarlet

(2) *Preparation from 2:6-Dichloro-*p*-phenylenediamine.*—2:6-Dichloro-*p*-phenylenediamine (1 part) dissolved in 40 parts of dry

acetone at  $-10^{\circ}$  was diazotised with 0.85 part of nitrous anhydride in a 10 per cent. acetone solution. The solution, which was stirred mechanically, became slightly paler in colour, and on the addition of 2 parts of acetic anhydride gave a dark grey, flocculent precipitate. This substance, which decomposed explosively at  $138^{\circ}$ , was very sensitive to light and darkened on exposure:

0.2000 gave 33.25 c.c.  $N_2$  at  $19^{\circ}$  and 759 mm.  $N=19.11$ .

$C_8H_5ON_2Cl$  requires  $N=18.25$  per cent.

This specimen of diazoimide, combined in pyridine with the following developers, gave the same colour reactions as those obtained in the foregoing preparation:

Developer.	Colour of azo-derivative.	Coloration with concentrated sulphuric acid.
$\beta$ -Naphthol .....	Orange-red	Scarlet
$\beta$ -Naphthylamine .....	Orange	Blue
$\alpha$ -Naphthol .....	Brownish-red	Green
$\alpha$ -Naphthylamine .....	Orange	Scarlet

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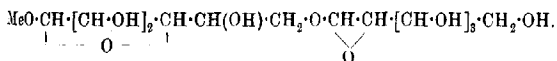
[Received, June 20th, 1918.]

#### XLVIII.—*A New Form of Methylgalactoside and its Conversion into Octamethyldigalactose and into a Methyldigalactoside.*

By MARY CUNNINGHAM.

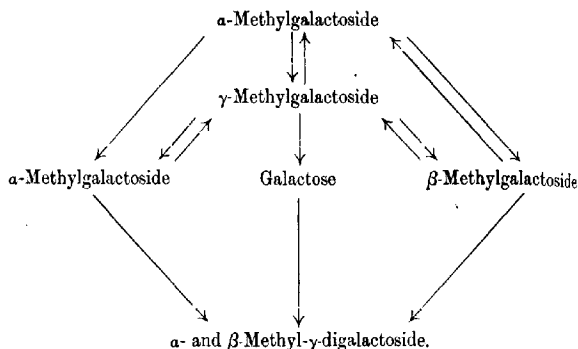
THE isolation of a new form of methylglucoside by Fischer (*Ber.*, 1914, **47**, 1980), and the detailed study of its derivatives by Irvine, Fyfe, and Hogg (*T.*, 1915, **107**, 524), naturally suggests the possibility that members of the dulcitol series of hexoses may also exhibit the same structural isomerism. Observations have, in fact, already been recorded indicating that galactose can react in a form other than the  $\alpha$ - and  $\beta$ -modifications, and recently all doubt on this point has been removed by the preparation of four galactose pentaacetates by Hudson and his co-workers (*J. Amer. Chem. Soc.*, 1916, **38**, 1223). The first mention of this unexpected isomerism occurs, however, in Fischer's original description of the methylhexosides (*Ber.*, 1895, **28**, 1174). By concentrating an acid methyl-alcoholic solution of the crystalline  $\alpha$ - and  $\beta$ -methylgalactosides, an amorphous product was obtained which Fischer regarded as a third form of methylgalactoside. The absence of analytical data

rendered complete identification of this substance impossible, and some years later Irvine and Cameron (T., 1905, **86**, 907) suggested that a methylated galactoside prepared by them and found to possess abnormal properties might be a derivative of the third isomeride referred to by Fischer. In this research, Irvine and Cameron isolated a syrupy form of methylgalactoside, which from its low specific rotation was at first regarded as consisting mainly of the  $\beta$ -modification. This particular methylhexoside is now shown to be a true methylgalactoside of the  $\gamma$ -series resembling  $\gamma$ -methylglucoside in its properties, but it is not identical with Fischer's amorphous product, which, as shown by analysis and a molecular weight determination, is a *methyldigalactoside*. The new form of methylgalactoside gives on methylation, followed by hydrolysis, tetramethyl  $\gamma$ -galactose, identical with the compound previously prepared by Irvine and Cameron (*loc. cit.*), and this sugar has now been found to possess the unique property of undergoing auto-condensation to give octamethyl  $\gamma$ -digalactose. The reaction in question proceeds spontaneously at the ordinary temperature and in the absence of any recognisable catalyst. This is, of course, a most unusual result, and, taken in conjunction with the formation, in somewhat similar circumstances, of a substituted disaccharide derivative from  $\gamma$ -methylglucoside (Irvine, Fyfe, and Hogg, *loc. cit.*), it serves to emphasise the extraordinarily reactive character of ethylene-oxide sugars. Moreover, it has been shown that the reaction which gives rise to methyldigalactoside also involves the presence—probably only transitory—of a variety of galactose conforming to this particular type of sugar. This conclusion seems warranted by the fact that the digalactoside, as shown by a study of its behaviour on hydrolysis, consists of the stable forms of methylgalactoside ( $\alpha$ - and  $\beta$ -) united to the unstable form of the sugar. The union involves the reducing group of the latter, and accordingly the structure of the complex is represented by the formula



A significant observation is that no structural modification of the digalactoside can be obtained by varying the form of methylgalactoside employed in its preparation. Thus, whether the starting point is an acid, methyl-alcoholic solution of pure  $\alpha$ -, pure  $\gamma$ -, or an equilibrium mixture of  $\alpha$ - and  $\beta$ -methylgalactosides, a compound having the same constants and properties and giving the same results on hydrolysis is formed in each case. The most prob-

able explanation of this rather surprising result seems to be that under the influence of acid methyl alcohol, any one form of methylgalactoside passes to an equilibrium mixture of the three isomerides  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and of these the unstable  $\gamma$ -variety is subsequently hydrolysed on concentration to give the reactive type of the sugar. This immediately combines with the stable hexosides to give a non-reducing complex, regeneration of  $\gamma$ -methylgalactoside being impossible owing to the removal of the alcohol. The course of the reaction would be represented by the following scheme:



These suggestions are, moreover, in accord with the results previously obtained by Irvine and Cameron (T., 1905, **66**, 907), who found that fully methylated hexosides of stable form could be heated at 110° to 150° without any hydrolysis occurring, the only change observed being an interconversion to an equilibrium mixture of the  $\alpha$ - and  $\beta$ -isomerides. In these experiments, the formation of the  $\gamma$ -variety was impossible owing to the presence of the methoxyl groups, so that the complicated reactions described above could not take place.

#### EXPERIMENTAL.

*γ-Methylgalactoside.*—Galactose was heated at 100° with methyl alcohol containing 0.25 per cent. of hydrogen chloride in essentially the way described by Fischer for the preparation of  $\alpha$ - and  $\beta$ -methylgalactosides, except that the acid was neutralised before removing the solvent. The neutralised solution deposited crystals of  $\alpha$ -methylgalactoside on slight concentration, and from the filtrate a viscid syrup was obtained on further heating. On the addition of ether, this syrup formed a semi-solid mass consisting for the

most part of  $\alpha$ - and  $\beta$ -methylgalactosides, but on triturating the mass with small quantities of absolute alcohol, some of the adhering syrup passed into solution and was removed by filtration. In this manner, a nearly colourless syrup of a non-reducing character was prepared which, in order to remove impurities, was dissolved in methyl alcohol and the solution fractionally precipitated by successive additions of ethyl acetate. The yield was 30 per cent. of the sugar used. For analysis, the syrup was dried to constant weight at 60°/20 mm. This method of preparation, it will be observed, differs considerably from that described by Fischer (*loc. cit.*) for the isolation of  $\gamma$ -methylglucoside, and it seems to point to the interesting conclusion that in the ordinary process of hexoside synthesis, the three modifications,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -, are produced together.

Found: C=42.94; H=7.3; OMe=15.7.

$C_7H_{14}O_6$  requires C=43.27; H=7.27; OMe=15.98 per cent.

The new compound thus isolated as a mixture of stereoisomerides showed the characteristic reactions of derivatives of the  $\gamma$ -series and gave  $[\alpha]_D +12.95^\circ$  in methyl alcohol and  $+25.9^\circ$  in water. It should be mentioned that attempts to prepare acetone derivatives similar to  $\gamma$ -methylglucosidemonoacetone were entirely unsuccessful.

*Hydrolysis of  $\gamma$ -Methylgalactoside.*— $\gamma$ -Methylgalactoside is somewhat more stable towards dilute acids than the corresponding glucoside, as it is necessary to carry out the hydrolysis with *N*/100-hydrochloric acid at 100°. The changes in optical activity observed are shown in Fig. 1, and it will be seen that the specific rotation increases without any irregularities until the value for galactose is reached, at the end of four and a-half hours. The continuity of the curve might at first suggest that only one of the two possible modifications of the ethylene-oxide type was present, but subsequent methylation showed the existence of the two varieties. The form of the curve does, however, prove that Fischer's amorphous product cannot be one of these  $\gamma$ -isomerides. This compound is more dextrorotatory than galactose itself, and if it were present, the curve would show a point above the specific rotation of galactose before the constant value was reached.

*Tetramethyl  $\gamma$ -Methylgalactoside.*— $\gamma$ -Methylgalactoside was methylated by the silver oxide method under the usual conditions, and the alkylation proceeded normally. After three methylations, the product was extracted with ether, and on distilling at 142–145°/12 mm., a colourless, mobile liquid was obtained having  $[\alpha]_D +3.98^\circ$  in alcohol. The value given by Irvine and Cameron for their abnormal form of tetramethyl methylgalactoside was

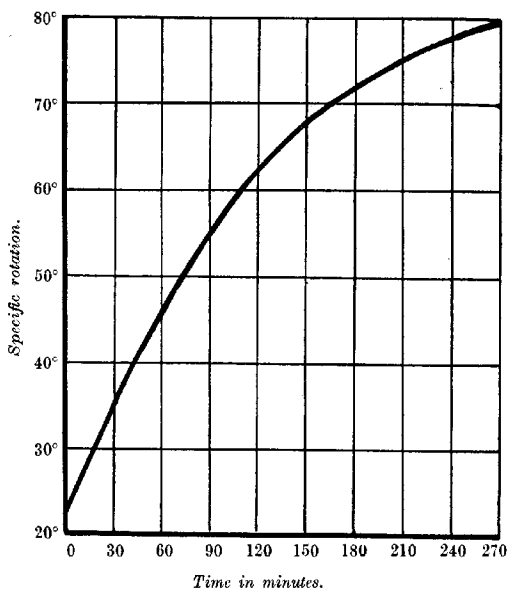


+4.06°, so that the two compounds are identical. Fractionation separated the distillate into two portions; the one boiling at 135°/12 mm. gave  $[\alpha]_D -4.3^\circ$ , and the other, boiling at 150°/12 mm., showed  $[\alpha]_D +8.8^\circ$ , but the analytical composition of each fraction was identical.

*Hydrolysis of Tetramethyl  $\gamma$ -Methylgalactoside, Tetramethyl  $\gamma$ -Galactose, and Octamethyl  $\gamma$ -Digalactose.*—The methylated galactoside is only completely converted into the corresponding

FIG. 1.

*Hydrolysis of  $\gamma$ -methylgalactoside.*

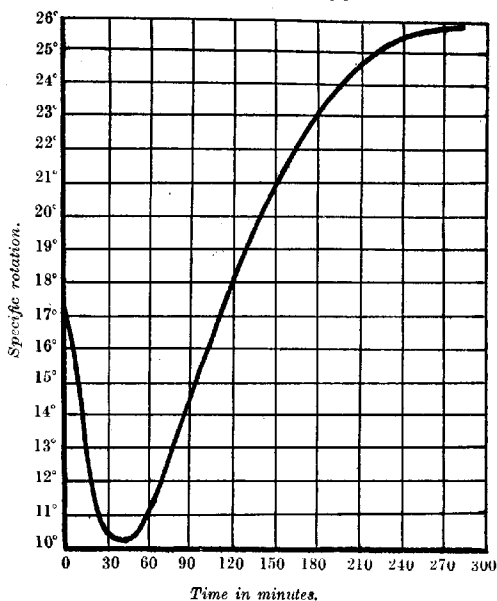


sugar by heating at 100° with *N*/100-hydrochloric acid for eight hours, and consequently hydrolysis experiments were carried out with *N*/10-acid at 100°. As shown on the accompanying curve (Fig. 2), the specific rotation falls initially and then rises, the constant value +25.9° being reached at the end of five hours. The specific rotation given by Irvine and Cameron (*loc. cit.*) for the methylated sugar was 26.1°, so that there was no doubt that tetramethyl  $\gamma$ -galactose was present, but as new and unexpected cases

of auto-condensation had recently been observed, the sugar, isolated as usual, was left to remain for some time before distillation with the idea that a disaccharide derivative might possibly be formed. After an interval of seven days, the syrup was distilled at the low pressure of the Gaede pump. The distillate (b. p.  $114-117^{\circ}/0.63$  mm.), which was a colourless syrup, had now lost the properties of a reducing sugar and acquired those of a glucoside. More-

FIG. 2.

*Hydrolysis of tetramethyl  $\gamma$ -methylgalactoside.*



over, the specific rotation had increased greatly, the values for  $[\alpha]_D$  in alcohol and water being  $+54.4^{\circ}$  and  $+75^{\circ}$  respectively. As was to be expected, the new compound reduced potassium permanganate solution instantaneously.

Found: C=52.2, 52.4; H=8.5, 8.7; OMe=57.1, 57.3.

$C_{20}H_{38}O_{11}$  requires C=52.86; H=8.4; OMe=54.6 per cent.

The analytical figures indicate that the compound is octamethyl-digalactose; but it is obviously not quite pure.

*Hydrolysis of Octamethyl  $\gamma$ -Digalactose.*—On heating a solution of the methylated disaccharide in  $N/10$ -hydrochloric acid at  $100^\circ$ , the specific rotation decreased, and at the end of eight and a-half hours reached the constant value  $+25.6^\circ$ , which agrees with the figure previously found for tetramethyl  $\gamma$ -galactose, and establishes the compound as essentially a disaccharide derivative.

*Methyldigalactoside (1) from  $\alpha$ - and  $\beta$ -Methylgalactosides.*—A solution of 10 grams of an equilibrium mixture of  $\alpha$ - and  $\beta$ -methylgalactosides in 50 c.c. of methyl alcohol was concentrated to a viscid syrup, which was dissolved in methyl alcohol and the solution filtered. Addition of absolute alcohol to the filtrate gave a white, amorphous product of an extremely deliquescent nature which, after remaining for some time in a vacuum, was dried to constant weight at  $70^\circ/20$  mm. The compound behaved as a glucoside to Fehling's solution, and gave  $[\alpha]_D$  in methyl alcohol  $+85.6^\circ$  and in water  $+101.1^\circ$ .

Found: C=43.88; H=6.9; OMe=9.05.

$C_{13}H_{24}O_{11}$  requires C=43.8; H=6.8; OMe=8.7 per cent.

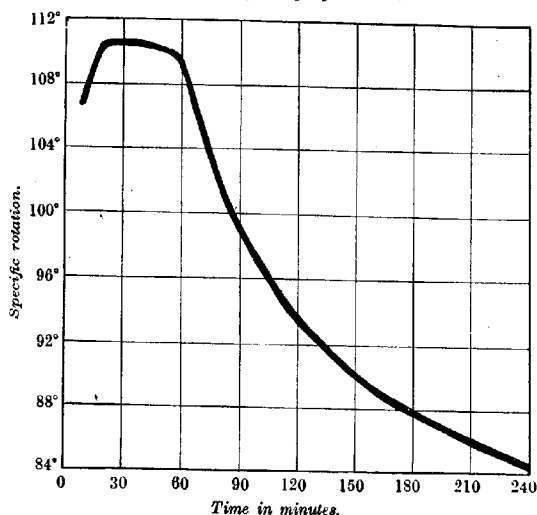
A molecular weight determination by the cryoscopic method gave M.W. = 341;  $C_{13}H_{24}O_{11}$  requires M.W. = 356.

An estimation by the ebullioscopic method could not be carried out, owing to the sparing solubility of the compound in any suitable solvent.

*Hydrolysis of Methyldigalactoside.*—The digalactoside showed the marked instability towards neutral potassium permanganate solution characteristic of ethylene-oxide compounds, so that it evidently contained one or more unstable linkings, and as these are ruptured by heating at  $100^\circ$  with  $N/100$ -hydrochloric acid, their number and position in the molecule of the digalactoside could be ascertained by following the course of the hydrolysis with the polarimeter. The specific rotation was found to increase and reached a constant value at the end of three hours, whilst the solution acquired reducing properties. This reduction was entirely due to the formation of galactose, as indicated by the fact that treatment with phenylhydrazine yielded galactosephenylosazone alone. At the same time, a methoxyl estimation carried out on the products isolated at this first stage of the hydrolysis showed that a hexoside was present. Hence the increase in specific rotation is not due to the formation of a disaccharide, but is occasioned by the liberation of  $\alpha$ -methylgalactoside,  $[\alpha]_D + 180^\circ$ . The molecule of the digalactoside therefore contains only one unstable linking, which is situated in one of the sugar residues, and the stability of the glucosidic methyl group shows that this portion of the molecule

retains the normal butylene-oxide structure. These observations are summarised in the constitutional formula given on p. 597. The maximum value for the optical activity is, however, less than that required for an equimolecular mixture of  $\alpha$ -methylgalactoside,  $[\alpha]_D + 180^\circ$ , and galactoside,  $[\alpha]_D + 81^\circ$ . This deficiency is most likely due to the presence of the practically inactive  $\beta$ -methylgalactoside, and the form of the rotation curve when the hydrolysis is carried out with  $N/10$ -hydrochloric acid supports this contention. The changes in specific rotation are shown in Fig. 3, and it will be

FIG. 3.  
*Hydrolysis of methyl digalactoside.*



observed that the rapid rise to the maximum value in the first twenty minutes is succeeded by a constant period of forty minutes, during which the decline in activity due to the hydrolysis of the  $\alpha$ -isomeride is balanced by the increase in activity occasioned by the more quickly hydrolysed  $\beta$ -form, whilst the marked fall in the next ten minutes indicates that this masking effect has now disappeared. The specific rotation then decreases regularly until the value for galactose is reached after four hours. This preparation of the digalactoside therefore undoubtedly consists of  $\alpha$ - and  $\beta$ -methylgalactosides in union with  $\gamma$ -galactose.

*Methyldigalactoside* (2) from  $\gamma$ -Methylgalactoside.— $\gamma$ -Methylgalactoside was treated in the same way as the mixture of  $\alpha$ - and  $\beta$ -methylgalactosides. The compound isolated gave the same values for the specific rotation as the previous preparation,  $+85.6^\circ$  in methyl alcohol and  $101.1^\circ$  in water. On hydrolysis with  $N/100$  hydrochloric acid at  $100^\circ$ , the specific rotation increased to the constant value  $+109.6^\circ$  at the end of three hours, and after the acid concentration had been raised to  $N/10$ , the same characteristic points were observed as before. The specific rotation remained constant for forty minutes, and then fell sharply to  $104.5^\circ$  in the next twenty minutes, after which it decreased steadily until the hydrolysis was complete.

*Methyldigalactoside* (3) from  $\alpha$ -Methylgalactoside.—In this experiment, a specimen of  $\alpha$ -methylgalactoside was used which had been several times recrystallised until entirely free from traces of either the  $\beta$ - or the  $\gamma$ -isomeride. The specific rotation of the digalactoside obtained was  $+100.9^\circ$  in water, and this increased on heating with  $N/100$ -hydrochloric acid at  $100^\circ$  to the maximum value  $110.3^\circ$  at the end of three hours. Thereafter the concentration of acid was changed as before, when the variations in activity previously described were again observed. The preparations of the digalactosides are therefore indistinguishable from each other.

I wish to express my indebtedness to Professor Irvine for valuable advice in carrying out this work.

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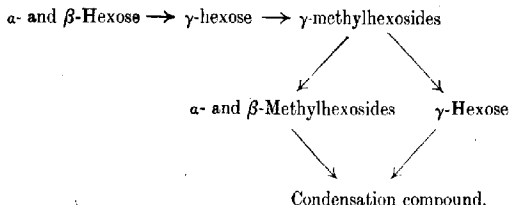
[Received, April 23rd, 1918.]

## XI.—The Application of the Auto-condensation Powers of $\gamma$ -Sugars to the Synthesis of Carbohydrate Complexes.

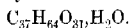
By MARY CUNNINGHAM.

THE preparation of  $\gamma$ -methylglucosidemonoacetone (Macdonald, T., 1913, 103, 1896; Irvine, Fyfe, and Hogg, T., 1915, 107, 524) and a comparison of the conditions under which the stable and unstable hexosides are formed suggest that the initial action of acid methyl alcohol on a reducing sugar may consist in transform-

ing a portion of it from the normal to the reactive form. This form of the sugar seems incapable of existence in the free state, and hence it would immediately combine with the alcohol to form a  $\gamma$ -methylhexoside. In the preceding communication it has been shown that if a solution of any one of the three isomeric methylgalactosides in acid methyl alcohol is concentrated, then a mixture of stereoisomeric condensation compounds results consisting of the stable hexosides united to  $\gamma$ -galactose. It seemed, therefore, not impossible that similar compounds might be formed by merely dissolving a reducing sugar in this reagent and concentrating the solution. The course of the anticipated reaction is represented by the following scheme:



It was, of course, recognised that as the reaction could not be readily controlled, the  $\gamma$ -sugar formed might condense either with the stable hexosides or with a preformed complex, thus giving rise to products of greater complexity than the methylidigalactoside referred to, or even to mixtures of different complexes. These ideas were realised in that compounds containing two or more sugar molecules were obtained, galactose and dextrose giving respectively a methyltetragalactoside and a methyltetraglucoside,  $C_{35}H_{44}O_{21}$ , whilst maltose yielded a methyltrimaltoside,



Compounds of a similar nature could not be prepared from fructose, as charring invariably occurred on concentrating a solution of the sugar in acid methyl alcohol, and, among the reducing disaccharides, lactose remained entirely unaffected by the reagent. The products behaved as glucosides towards Fehling's solution and showed the characteristic reactions of  $\gamma$ -compounds, whilst the results obtained on hydrolysis indicate that they are constituted similarly to methylidigalactoside, the glucosidic methyl group being attached to a sugar residue retaining the normal butylene-oxide structure, whilst the remaining sugar residues conform to the ethylene-oxide type. It should be mentioned that estimations of methoxyl have been chiefly relied on in establishing the degree of

complexity of these derivatives. Elementary analysis is obviously of little assistance, and the presence of so many hydroxyl groups rendered accurate determinations of molecular weight impossible, especially as water was the only solvent that could be employed.

### EXPERIMENTAL.

The same method of preparation was adopted in each case. Ten grams of finely powdered sugar were added gradually to 50 c.c. of methyl alcohol containing 0.25 per cent. of hydrogen chloride, and the mixture was gently warmed, if necessary, to hasten solution. The solution was then concentrated on a steam-bath to a viscid syrup, which was dissolved in a small quantity of methyl alcohol, and, after the solution had been filtered, absolute alcohol was added, which precipitated the complex as a white, amorphous product. This was collected with difficulty, owing to the deliquescent nature of these compounds, and finally dried to constant weight at 70–80°/12 mm.

*Methyltetragalactoside*.—Found: C=44.16; H=6.8; OMe=4.3, 4.0.

$C_{25}H_{44}O_{21}$  requires C=44.12; H=6.5; OMe=4.5 per cent.

$[\alpha]_D$  in water = 94.0° ( $c=1.6590$ ).

*Hydrolysis of Methyltetragalactoside*.—On heating at 100° with *N*/100-hydrochloric acid, the specific rotation increased to the constant value +108.5° at the end of five hours. Galactosephenyl-osazone alone was isolated at this stage, so that the increase in optical activity is probably due to the presence of  $\alpha$ -methylgalactoside. Thereafter, the acid concentration was raised to *N*/10, and some of the polarimetric changes observed are shown below:

Initial specific rotation.....	+108.5°
After 320 minutes at 100° .....	108.5
" 340   "   " .....	106.0
" 360   "   " .....	100.0
" 420   "   " .....	94.0
" 540   "   " .....	86.8 (constant)

As in the case of methylbigalactoside, the presence of  $\beta$ -methylgalactoside seems established by the fluctuations in activity recorded in the first sixty minutes. The final optical value when corrected for the calculated weight of sugar formed on the basis of the suggested formula for the compound becomes +82.0° (galactose = +81.0°).

*Methyltetraglucoside*.—Found: C=43.5; H=6.6; OMe=4.96.

$C_{25}H_{44}O_{21}$  requires C=44.12; H=6.5; OMe=4.5 per cent.

$[\alpha]_D$  in water = 98.1° ( $c=0.9070$ ).

*Hydrolysis of Methyltetraglucoside.*—The specific rotation increased on partial hydrolysis with  $N/100$ -acid at  $100^\circ$  to the value  $+104.5^\circ$  at the end of sixty minutes, and then declined steadily, the final value,  $+87.5^\circ$ , being reached at the end of four hours. The initial rise and subsequent fall probably indicate, as in the case of the galactose derivative, that both  $\alpha$ -methylglucoside,  $[\alpha]_D +157^\circ$ , and  $\beta$ -methylglucoside,  $[\alpha]_D -33^\circ$ , are present. On completing the hydrolysis with  $N/10$ -acid, the optical activity continually declined, reaching the constant value  $+57.3^\circ$  after heating for a further six hours. Calculating on the above formula, this gives  $+54.1^\circ$  as the actual value for the specific rotation, which again is not far removed from the theoretical number  $+52.5^\circ$ .

*Methyltrimaltoside.*—This compound, even after drying to constant weight at  $70^\circ/40$  mm., retained a molecule of water, which was only removed on further heating at  $100^\circ/40$  mm.

Found: C=43.0, 43.0; H=6.6, 6.7; OMe=3.6, 3.5;  $H_2O=1.5$ .  $C_{37}H_{64}O_{21}, H_2O$  requires C=43.4; H=6.5; OMe=3.0;  $H_2O=1.7$  per cent.

$[\alpha]_D$  in water  $+124.0^\circ$  ( $c=1.057$ ).

*Hydrolysis of Methyltrimaltoside.*—After heating with  $N/100$ -hydrochloric acid at  $100^\circ$  for three hours, the specific rotation had declined to the constant value  $+113.6^\circ$ , when maltosephenylosazone was isolated, but on further hydrolysis with  $N/10$ -acid the activity continued to decline, showing that both the maltoside and the maltose were undergoing hydrolysis. The final value,  $+56.8^\circ$  (corrected,  $+53.7^\circ$ ), was obtained at the end of ten hours.

The author desires to express her thanks to Professor Irvine for the advice and assistance which she has received.

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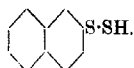
[Received, March 12th, 1918.]



### L.—The Preparation of a New Type of Organic Sulphur Compound.

By GERALD NOEL WHITE.

THE compound which forms the subject of this paper is a representative of a class of compounds which, so far as can be ascertained, has hitherto eluded isolation, being a derivative of hydrogen persulphide,  $\text{H}_2\text{S}_2$ , in the form of  *$\beta$ -naphthylthiosulphoxylic acid*:



It is highly probable that compounds of this type are produced as intermediate products in a number of chemical processes. In particular, the production of the sulphide dyes in all probability involves the formation of analogous derivatives of hydrogen disulphide.

The compound in question is produced by gently heating together molecular quantities of  *$\beta$ -naphthyl disulphide*, sodium sulphide crystals, and pure sulphur. After complete solution of the sulphur in the aqueous sodium sulphide, the naphthyl disulphide passes slowly into solution with continued heating to about  $80^\circ$ .

On cooling, glistening lamellæ of the *sodium* salt, which is very readily soluble in water, crystallise out. Purification is difficult, but after pressing on a porous plate, the most satisfactory method is to dissolve the sodium salt in alcohol and precipitate it with benzene.

For analysis, a portion of the sodium salt prepared in this way was treated with aqueous hydrochloric acid. The free acid was dissolved in alcohol and precipitated with water; this process was repeated three times and the product dried in a desiccator:

0.1757 gave 0.4044  $\text{CO}_2$  and 0.0569  $\text{H}_2\text{O}$ .  $\text{C}=62.8$ ;  $\text{H}=3.6$ .

0.1136 gave 0.2827  $\text{BaSO}_4$ .  $\text{S}=34.1$ .

$\text{C}_{10}\text{H}_7\text{S}_2$  requires  $\text{C}=63.1$ ;  $\text{H}=3.2$ ;  $\text{S}=33.7$  per cent.

With lead acetate, a deep orange precipitate is obtained, which darkens to scarlet on keeping, and ultimately changes to deep brown or black by decomposition to lead sulphide.

If this reaction is allowed to proceed in boiling alcohol, and the clear solution decanted quickly, crystals of  *$\beta$ -naphthyl disulphide* are formed on cooling which are remarkable for their purity. A study of this reaction failed to detect any deposition of sulphur as should result from the decomposition of a normal

lead salt, and it seems probable that the alcohol used in the reaction may act as a reducing agent, which would explain this observation.

At present, however, the evidence is insufficient to do more than indicate the possible course of the reaction.

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[Received, June 11th, 1918.]

### LI.—*Double Carbonates of Sodium and Potassium with the Heavy Metals.*

By MALCOLM PERCIVAL APPLEBEY and KENNETH WESTMACOTT LANE.

THE combination of alkali carbonates with carbonates of the heavy metals to form crystalline double salts has been long known, many of these compounds having been prepared by Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75) by digesting the precipitated metallic carbonate with excess of a concentrated solution of the alkali carbonate. Double carbonates of cobalt, nickel, zinc, and magnesium with potassium, and of copper, magnesium, cobalt, nickel, and zinc with sodium, were thus prepared, whilst several double bicarbonates were obtained in a similar manner. Owing to the method of preparation adopted, Deville's compounds must have been contaminated with normal and basic metallic carbonates, but his products were sufficiently pure to make possible a general characterisation of this group of substances. A somewhat more satisfactory method of preparation was adopted by Reynolds (*T.*, 1898, **73**, 262), who ground the solid acetate of the metal with a concentrated solution of potassium carbonate. Under these conditions, complete solution takes place, and the crystalline double carbonate is subsequently deposited in a fairly pure state. In this way, Reynolds succeeded in obtaining the double carbonate of copper and potassium which Deville had failed to prepare owing to its great solubility. The analyses of Reynolds's copper compounds show rather high values for the copper content, and suggest the presence of basic carbonate. Gröger (*Ber.*, 1901, **34**, 429) afterwards demonstrated the advisability of adding bicarbonate to the alkaline carbonate solution, a modification which, as was pointed out by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 71), represses the hydrolytic dissociation of the copper carbonate. The potassium and sodium copper carbonates prepared by Gröger never-

theless contained considerable amounts of basic carbonate, the potassium salt being particularly impure. This was, however, probably due to the subsequent treatment of the salts.

The nature of the deep blue solutions from which the copper salts are deposited has been examined by Luther and Krinjaví (*Zeitsch. anorg. Chem.*, 1905, **46**, 170), who proved by transport experiments the presence of a deep blue complex negative ion containing copper. The conditions under which crystallisation of double salts from such solutions takes place have also been discussed by Deville and by Gröger. No quantitative study of these conditions has yet, however, been attempted, although the case is one of particular interest, since it relates to a double salt of which one constituent is practically insoluble in water. The authors therefore undertook a study of the solubility equilibria in the case  $\text{Na}_2\text{CO}_3\text{--Na}_2\text{Cu}(\text{CO}_3)_2\text{--CuCO}_3$ , which is typical of double salt equilibria of this kind. It was hoped that a parallel investigation of the equilibria in the formation of the potassium cobalt compound would be of interest. Unfortunately, owing to the difficulties of analysis in the latter case and to the enforced suspension of the work under present conditions, it has not been found possible to bring this part of the investigation to a satisfactory conclusion. The present communication therefore deals almost entirely with the sodium copper carbonate equilibrium.

#### *Preparation and Properties of the Double Salts.*

The salts prepared for the purpose of this investigation were all obtained by a method which, whilst not giving so good a yield as could be obtained by Reynolds's method, was preferable for the purpose in view, since it gave products of greater purity, analysis showing that the amount of basic carbonate present was small.

*Sodium Copper Carbonate.*—A solution was prepared containing about 100 grams of sodium carbonate (anhydrous) and 40 grams of sodium bicarbonate in a litre. To this solution, at a temperature of about  $50^\circ$ , a concentrated solution of cupric acetate was added from a burette with a fine point, the liquid being stirred continually during the addition. A clear, deep blue solution quite free from suspended basic carbonate is obtained in this way. The amount of cupric acetate solution to be added is found by trial; if too much is added, precipitation of basic carbonate occurs; if too little, there is no crystallisation. The solution is filtered and left to remain overnight, when a deposition of well-formed crystals of the double salt takes place. These are collected, rapidly washed with

pure alcohol, and dried in a desiccator. The mother liquor can be used for a further preparation, and gives a rather better yield.

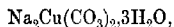
The salt, which crystallises in needles or rosette-like agglomerations, dries to a constant weight in a desiccator. It is, in fact, a more stable substance than might be expected, since microscopic examination fails to show any alteration in the transparency of the crystals after they have been kept at the temperature of boiling water for a considerable time. At higher temperatures, the substance loses water and carbon dioxide, passing through a stage when it has a purple colour, and giving finally a mixture of cupric oxide and sodium carbonate. It is decomposed by water, but dissolves in and can be recrystallised from a concentrated solution of sodium carbonate containing bicarbonate. This observation, which is in direct contradiction to the experience of Gröger (*loc. cit.*), has been fully established by repeated tests.

The copper in the compound was determined by the sulphide method and also electrolytically, the sodium as sulphate after precipitation of the copper. Carbon dioxide and water were estimated directly in the usual manner.

Found: Cu=22.05; Na=16.05;  $\text{CO}_3$ =42.52;  $\text{H}_2\text{O}$ =19.62.

$\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$  requires Cu=22.40; Na=16.21;  $\text{CO}_3$ =42.37;  $\text{H}_2\text{O}$ =19.02 per cent.

It will be seen that the substance has the formula



as was found by Deville, Gröger, and Wood and Jones (*loc. cit.*). The amount of water of crystallisation in this salt is somewhat anomalous, as the large number of double carbonates of potassium investigated by Reynolds, and the sodium cobalt compound to be described later, all crystallise with four molecules of water.\*

*Sodium Cobalt Carbonate.*—This substance was prepared in exactly the same manner as the copper compound, except that the cobalt was added in the form of nitrate solution. The double salt crystallises in crusts of fine crystals of a very bright reddish-purple colour. It can be recrystallised from a solution of sodium carbonate and bicarbonate, but it is difficult to obtain well-formed crystals.

The salt was analysed by dissolving a weighed quantity in excess of standard acid and titrating with standard alkali, using methyl-orange as indicator. The colour of the solution is not sufficiently intense to affect the accuracy of this determination, which gives the total basic equivalent of the sodium and cobalt in the compound. Another weighed sample is then ignited until it is completely con-

\* The potassium copper salt can also be obtained anhydrous and with one molecule of water, but not with three.

verted into a mixture of cobalt oxide and sodium carbonate, of which the latter can be extracted with hot water and estimated by titration. This gives the percentage of sodium in the compound and the percentage of cobalt by comparison with the determination of total basic value. The sodium was also determined as sulphate (a). The water was determined in the usual way and the carbon dioxide by difference.

Found: Co = 20.42; Na = 15.03, 15.26(a);  $\text{CO}_2$  = 40.79;  $\text{H}_2\text{O}$  = 23.64.

$\text{Na}_2\text{Co}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$  requires Co = 19.85; Na = 15.52;  $\text{CO}_2$  = 40.38;  $\text{H}_2\text{O}$  = 24.25 per cent.

The substance evidently has a formula corresponding with the double potassium salts described by Reynolds, and is therefore unlike the sodium copper carbonate, which has only three molecules of water of crystallisation. Deville also obtained a double sodium cobalt carbonate with ten molecules of water, but this substance was not formed under the conditions described in this paper.

*Potassium Cobalt Carbonate.*—This salt is obtained in an analogous manner to those previously described, the solution used for the preparation containing about 400 grams of potassium carbonate and 100 grams of potassium bicarbonate per litre. On addition of cobalt nitrate solution, a dark, reddish-purple solution is obtained very similar in appearance to that from which the sodium salt is deposited. The crystalline double salt is, however, different in habit and in appearance from the corresponding sodium compound. The crystals are well formed and do not mass together in compact crusts. They present the appearance of six-sided tables which have not the bright purple tint of the sodium salt. Large crystals formed by evaporation of solutions saturated with the double salt have a red colour resembling ordinary cobalt compounds, whilst the smaller crystals deposited from the purple solutions are a lighter red, or in some cases a pale pink. The differences in colour between different specimens at first led to the belief that the cobalt potassium compound occurred in several forms differing either in composition or in crystalline form. Repeated analyses and measurements of solubility failed, however, to show any difference between the differently coloured specimens, nor did either the red form or the pink form grow at the expense of the other when both were kept in contact with a saturated solution for several months. The authors are therefore bound to conclude that the differences of colour referred to are not due to differences of composition, structure, or crystalline arrangement. They are probably to be explained by occlusion of different amounts of some colloidal substance, such as cobalt

carbonate. This conclusion is supported by the observation that increase in the concentration of bicarbonate in solution tended to favour the production of the lighter coloured variety. The effect is probably quite parallel with the well-known changes in the colour of many metallic salts when crystallised from solutions of varying acidity; these changes have been shown to be due to the occlusion of varying quantities of metallic hydroxides under different conditions.

Analysis by the method used for the sodium cobalt compound gave:

Found: Co=17.85; K=24.05;  $\text{CO}_3$ =21.60;  $\text{H}_2\text{O}$ =36.50.

$\text{K}_2\text{Co}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$  requires Co=17.91; K=23.72;  $\text{CO}_3$ =21.89;

$\text{H}_2\text{O}$ =36.45 per cent.

This substance also clearly belongs to the normal type with four molecules of water of crystallisation, as was previously found by Reynolds.

Both the sodium and potassium cobalt salts have properties very similar to those of the sodium copper carbonate. They are quite stable in the cold, but lose water and carbon dioxide on heating. They are decomposed by water, but, like the copper compound, can be recrystallised from concentrated solutions of alkali carbonate and bicarbonate.

#### *Formation of the Double Salts.*

The formation of the double salts from the intensely coloured solutions has already excited some interest. Deville remarked upon the deep colour of the solutions, and doubted whether this colour could possibly be due to the small quantity of double carbonate which in the solid state is not more highly coloured than ordinary copper salts. A very striking experiment illustrating Deville's argument consists in acidifying a solution of the double carbonate containing 0.1 to 0.2 gram of copper per litre. This solution, which is bright blue, becomes almost colourless when the complex ion is destroyed by acidification, and even the addition of ammonia only produces a colour very much fainter than that of the original solution. Deville was so much impressed with the intense colour of the solutions that he regarded it as possible, if not probable, that the solutions contained some substance much more intensely coloured than the double carbonate into which it was slowly transformed during the crystallisation of the latter.

Other phenomena now to be discussed give considerable support to Deville's hypothesis. The crystals of the double salt are formed slowly from the solution when the latter has been kept for several hours, but the solution is not supersaturated in the ordinary sense.

This is shown by the fact that addition of crystalline nuclei does not appreciably hasten the separation. Gröger, who noted this phenomenon, also describes a remarkable experiment, which the authors have been unable to confirm. According to him, if a solution supersaturated with sodium bicarbonate is used in the preparation of the copper solution, addition of the crystalline double salt brings about no crystallisation, but sowing with a fragment of sodium bicarbonate not only induces crystallisation of the bicarbonate itself, but also brings about the rapid separation of the double salt along with it. This would constitute a remarkable type of supersaturation; attempts to repeat the experiment, however, never led to the result described, only bicarbonate being obtained as solid phase, whilst no appreciable fall in copper concentration took place.

It was thought that evaporation or absorption or loss of carbon dioxide might be a determining factor. Experiments were therefore entered on to test these points, but the results were entirely negative. Whether the solutions were left to crystallise in the open, in sealed flasks, or in a desiccator connected to a Kipp's apparatus for carbon dioxide, no appreciable difference in the rate of crystallisation was observed. It is therefore tentatively suggested that the behaviour of the solutions is due to one of the following causes:

(1) The rate of crystallisation is very small, and there are no stable supersaturated solutions.

(2) An intermediate compound is formed in the solutions which changes only slowly into the practically insoluble double salt.

In the latter case, the change from intermediate compound to double salt is reversible, since the double salt can be recrystallised from a solution of carbonate and bicarbonate.

#### *The Solubility Equilibria.*

. In undertaking this investigation, the authors were faced at the outset with the difficulty that solutions of the double salts are unstable in absence of bicarbonate. Repeated attempts to obtain a solution saturated with sodium carbonate decahydrate and with the sodium copper carbonate in absence of bicarbonate all led to failure. When the solids were stirred in a constant-temperature bath at 18°, a blue solution was obtained, but decomposition with precipitation of basic compounds always occurred before the experiment had proceeded a sufficiently long time to ensure the attainment of equilibrium. It was therefore decided that the work must be carried out exclusively with solutions containing bicarbonate.

In many respects, the simplest plan and that promising results of most interest was to work with solutions saturated with sodium carbonate or with sodium bicarbonate, and the determinations made by the authors relate only to such solutions. The equilibria investigated are therefore those of (1) sodium copper carbonate and sodium bicarbonate with solutions containing increasing quantities of sodium carbonate; (2) sodium copper carbonate and sodium carbonate decahydrate with solutions containing decreasing quantities of bicarbonate. In each of these regions we are dealing with a system univariant at constant temperature with two solid phases. At the point of intersection we have at constant temperature a non-variant system with three solid phases.

The concentration of copper in the equilibrium solutions is in all cases very small in comparison with the concentrations of the sodium salts. The latter may consequently be considered as influenced only to an inappreciable extent by the presence of copper. The determinations therefore serve also to characterise the equilibrium of sodium carbonate and sodium bicarbonate at the temperature of experiment. They may be compared with the results of McCoy and Test (*J. Amer. Chem. Soc.*, 1911, **33**, 473) at 25°.

The solutions were prepared in a stirring-bottle closed with a mercury seal and maintained at 18° by means of a constant-temperature bath regulating to 0.02°. The time allowed for equilibrium to be established was never less than forty hours, preliminary experiments having shown that this was a satisfactory minimum period. When saturation was complete, the stirrer was stopped and the solution was allowed to settle. The stirrer was then removed and replaced by an inverted filter, through which the saturated solution was blown into a clean flask, from which samples were taken for analysis. Filtration of the solutions was necessary, as in some cases a solid substance, probably a basic carbonate, was present in a state of very fine suspension.

The concentration of copper in the solutions was found by direct titration of the solutions with a potassium cyanide solution, standardised against alkaline copper solutions of known strength, due allowance being made for the variation in the titre of the solutions occasioned by variation in bicarbonate concentration. The cyanide titration of these solutions is much sharper than in the case of ammoniacal copper solutions of equal copper content (*Analyst*, 1918, **43**, 268).

The carbonate and bicarbonate were determined by dilution of the solutions by means of carefully standardised pipette and flask, and titration by Winkler's method. A modification of this method



which proved serviceable consisted in running in  $N/10$ -sodium hydroxide solution until the bicarbonate was almost completely changed into carbonate, the amount necessary being found by a preliminary trial. Excess of neutral barium chloride solution and a drop of phenolphthalein were then added, and the titration with sodium hydroxide was completed. This modification is preferable in point of convenience to Winkler's method of adding excess of sodium hydroxide, then adding barium chloride and phenolphthalein, and titrating back, and appears to be quite as accurate, although, of course, several titrations of each solution must be carried out. If the quantity of sodium hydroxide solution first added is sufficiently near the quantity required for complete conversion (within 0.2 or 0.3 c.c.), there appears to be no difficulty occasioned by the decomposition of the barium bicarbonate which must be formed on adding barium chloride.

The following tables give the results of the several experiments made with the sodium copper solutions (table I) and with the potassium cobalt solutions (table II). No determinations of the cobalt content of the latter solutions are given, as sufficiently trustworthy values were not obtained at the time when the experiments were interrupted. The concentration of cobalt in the equilibrium solutions was in the neighbourhood of 0.1 to 0.2 gram per litre, and appeared to pass through a minimum value at a concentration of potassium carbonate equal to about 200 grams per litre. A similar variation is not found in the case of the sodium copper compound, with which the copper content of the equilibrium solutions increases continually with increase of the carbonate concentration.

TABLE I.

No. of experi- ment.	Hours stirring.	Solid phases.	$\text{Na}_2\text{CO}_3$ grams/ litre.	$\text{NaHCO}_3$ grams/ litre.	Cu grams/ litre.
1	48	$\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{NaHCO}_3$	9.27	87.79	—
2	140		11.08	86.45	0.0509
3	50		11.29	86.75	—
4	50		13.44	85.27	0.0542
5	50		37.36	78.63	—
6	100		61.32	74.18	—
7	100		62.36	72.65	0.0870
8	100		96.68	65.31	0.1061
9	50		99.30	64.10	0.1061
10	70		152.63	56.24	0.1411
11	50		168.75	53.60	0.1553
12	50	$\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ $\text{NaHCO}_3$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	185.02	53.77	—
13	50	$\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	193.13	17.64	—
14	50		195.57	7.48	—
15	50		197.08	18.94	0.257

TABLE II.

No. of experi- ment.	Hours stirring.	Solid phases.	K <sub>2</sub> CO <sub>3</sub> , grams/ litre.	KHCO <sub>3</sub> , grams/ litre.
1	120	K <sub>2</sub> Co(CO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O and KHCO <sub>3</sub>	13.3	280.6
2	70		14.85	282.5
3	50		25.5	272.4
4	240		47.5	262.3
5	100		103.2	237.0
6	70		114.1	230.7
7	40		125.1	227.6
8	50		145.7	219.0
9	120		166.8	203.2
10	120		220.0	181.0
11	120		289.4	158.9
12	70		309.2	151.3
13	40		453.5	108.4
14	70		607.7	68.9
15	120		643.0	64.1
16	120		704.3	54.6
17	120	K <sub>2</sub> Co(CO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, KHCO <sub>3</sub> and K <sub>2</sub> CO <sub>3</sub> ·2KHCO <sub>3</sub> ·3H <sub>2</sub> O	800.2	43.1
18	120	K <sub>2</sub> Co(CO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O and K <sub>2</sub> CO <sub>3</sub> ·2KHCO <sub>3</sub> ·3H <sub>2</sub> O	805.1	40.9
19	170	K <sub>2</sub> Co(CO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O and K <sub>2</sub> CO <sub>3</sub> ·2KHCO <sub>3</sub> ·3H <sub>2</sub> O	822.8	35.0
20	170	K <sub>2</sub> Co(CO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O and K <sub>2</sub> CO <sub>3</sub> ·2KHCO <sub>3</sub> ·3H <sub>2</sub> O	825.8	33.1
21	100	K <sub>2</sub> Co(CO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O and K <sub>2</sub> CO <sub>3</sub> ·2H <sub>2</sub> O	836.2	12.2
22	170		840.8	5.9

These results are represented graphically in Figs. 1 and 2. Fig. 1, which also contains McCoy and Test's results for the sodium carbonate-bicarbonate equilibrium at 25°, shows no sign of a break corresponding with the double compound Na<sub>2</sub>CO<sub>3</sub>·NaHCO<sub>3</sub>·2H<sub>2</sub>O (trona) at 18°. It is therefore probable that this compound ceases to be stable in contact with solutions at some temperature between 18° and 25°.

In the course of the solubility experiments, it was noted that a distinct change in the appearance of the solid phase occurred in passing along the bicarbonate curve. The bicarbonate used in these experiments was the usual micro-crystalline variety, and this form appeared to suffer no change when left in the stirring bottle in contact with solutions ranging from pure bicarbonate to a point on the curve corresponding with about 70 grams of carbonate per litre. Beyond this point, the solid phase becomes transformed into well-formed, transparent crystals. These crystals are nevertheless pure anhydrous bicarbonate, as was established by repeated analyses. It is possible that a polymorphic change takes place, but in view of the fact that the solubility curve shows no break, and seeing that all attempts to obtain evidence of a definite transition point failed completely, the authors are inclined to think that the pheno-

menon is not to be explained by polymorphism. This opinion is supported by the absence of any clear distinction between the two

FIG. 1.

Upper curve, McCoy and Test, 25°  
Lower „ Applebey and Lane, 18°.

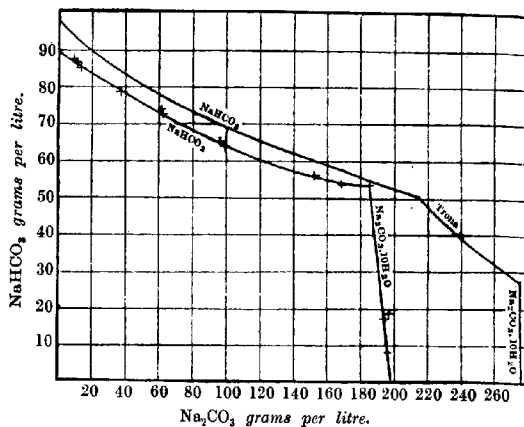
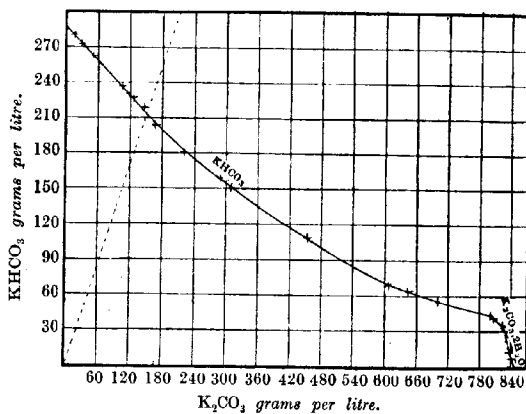


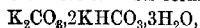
FIG. 2.



kinds of crystals when examined under the polarising microscope. Probably the conditions of the solubility equilibrium in presence

of considerable quantities of sodium carbonate are such as to facilitate the growth of the crystals.

Fig. 2, which is the corresponding diagram for potassium carbonate and bicarbonate, shows clear evidence of a double compound. This substance, the region of stability of which is very limited at 18°, is doubtless identical with the compound obtained by Bauer (*Ber.*, 1883, **16**, 1143) during the evaporation of bicarbonate solutions on a large scale in a mineral water factory. This salt was carefully analysed, and was examined crystallographically by Rammelsberg, but all attempts to obtain it synthetically have up to the present failed. Its formula is



and, as the figure shows, it is only obtainable in equilibrium with a very limited range of solutions, which are very different in composition from the double salt itself.

The determinations of copper concentration in the equilibrium solutions lie on a smooth curve showing a steady increase with increase in the concentration of sodium carbonate. The copper determination of experiment 15 alone lies considerably above the curve. This point is the only determination of copper concentration in a solution in equilibrium with sodium carbonate decahydrate as solid phase, and seems to show that the rapid decrease in the bicarbonate concentration along the decahydrate curve brings about an increase in the copper content. Experiment 15 is, however, not very satisfactory, as the solution appears to have been somewhat supersaturated with carbonate owing to failure of the regulation of temperature, and the corresponding point lies at a considerable distance from the curve in Fig. 1 which connects the other points. The authors therefore content themselves with noting the observation, but lay no stress on its interpretation.

#### *Discussion of Results.*

The experimental results set forth above have several features of interest which throw some light on the nature of the equilibria involved. In the first place, it is noteworthy that the curve of copper concentrations does not approach the solubility of copper carbonate in water, which is negligibly small, as the concentration of sodium carbonate decreases, but the curves of solubility of copper carbonate and double salt appear to intersect at a copper concentration of about 0.045 gram per litre. This is unlike the normal case of double salt equilibrium in which the solubility of each component is lowered by the addition of the other. Assuming that this abnormal rise of solubility of copper carbonate in the presence

of sodium carbonate is due to the formation of the complex ion  $\text{Cu}(\text{CO}_3)_2$ , it is easily shown that the first effect of sodium carbonate must be to depress the solubility of the other component, the solubility passing through a minimum, and subsequently rising on addition of further quantities of the sodium salt. The investigation of this curve forms no part of the present investigations. It may be noted, however, as a point of interest, that by the application of the mass-action law, which is possibly justifiable in that only very dilute solutions are under consideration, it can be readily established that the position of the minimum solubility is given by the condition.

$$[\text{Cu}^{++}] = [\text{Cu}(\text{CO}_3)_2]^{1/2}.$$

Passing now to the consideration of solutions saturated with the double salt,  $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ , the results obtained in the present work are again at variance with the normal behaviour of double salts in that the increase of concentration of one component brings about an increase in the concentration of the other, the curve apparently rising throughout its whole course. This abnormal behaviour must, as in the case of the solubility of copper carbonate itself, be occasioned by the formation of a new constituent in the solution which removes copper from the solution equilibrium of the double salt, and so leads to an increase in its apparent solubility. The increasing solubility of the double salt with rising concentration of sodium carbonate thus constitutes a direct experimental proof of the view held by Deville that the copper in these solutions was largely present in some form chemically different from the salt which crystallises out.

Turning now to the identification of the dissolved substance, which is thus the parent of the crystalline double carbonate, a little consideration will show that if the substance is an ionisable one, the complex copper ion which forms the negative part must consist of a more heavily carbonated species, such as  $\text{Cu}(\text{CO}_3)_4^{4-}$ ; the concentration of such an ion would increase with increasing concentration of carbonate. On the other hand, if such ions are present, it is very remarkable that double salts containing more than one equivalent of alkali carbonate to one of metallic carbonate never crystallise out of any of these alkali metallic carbonate solutions.

The authors are, however, of opinion that the true explanation of the solubility phenomena is to be found in the presence of a large proportion of the copper in the form of a colloidal substance, probably a normal or basic copper carbonate. This view accounts for the contrast between the colour of the solutions and that of the crystalline double salts, and is supported by the fact that

coagulation can certainly be brought about, although with difficulty, by the addition of much sodium phosphate to the solutions. The possibility that the solutions are of a colloidal nature has already been considered and rejected by Luther and Kršnjavi (*loc. cit.*) on the evidence of their transport experiments, and also because the solutions can diffuse through a parchment membrane. It appears, however, that such arguments, whilst they prove the presence of complex negative ions containing copper, do not at all exclude the simultaneous presence of a positive colloid, which may, in fact, be much greater in amount than the complex ions. In fact, it is obvious that when a solution contains a colloidal substance in kinetic equilibrium with crystalloids, the colloid will diffuse through an animal membrane by first changing into the dialysable form, the colloidal form being again obtained on the other side of the membrane by the reverse change. The passage of such a solute through a membrane will doubtless be slow in comparison with the rate of dialysis of crystalloids, but when the above conditions are fulfilled, such passage must take place. The escape of colloid normally comes to an end after a small quantity has passed, owing to the disappearance of some crystalloid factor on which the change to crystalloid form depends. An example which will make the argument clear may be found in ferric chloride. A solution of this substance may be regarded as made up of colloidal ferric hydroxide, ferric ions, and hydrogen and chlorine ions. In the dialyser, the ions, including the ferric ions, immediately begin to diffuse out, and diffusion of ferric ions will, in fact, continue as long as chlorine ions remain in the solution. The concentration of chlorine ions in such a solution is, however, not very great, and their escape is fairly rapid. The result is that escape of ferric ions soon comes to an end. In the case of the alkaline copper solutions, however, the crystalloid and diffusible substance,  $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ , is constantly regenerated, since the solutions contain much sodium carbonate, which takes a considerable time to escape from the dialyser. The escape of copper is therefore more pronounced than that of iron from a ferric chloride solution, and, in fact, is so favoured by the presence of excess of sodium carbonate that the solution simulates the behaviour of a simple crystalloid.

It is perhaps worth noting that Luther and Kršnjavi remark that the movement of the coloured boundary in their transport experiments was very slow. This may to some extent be due to the conversion of the complex ions which have crossed the boundary into the positive colloid, which travels in the opposite direction by cataphoresis.

In conclusion, the authors wish to express their indebtedness to Mr. D. H. Nagel and to Mr. D. L. Chapman for much valuable assistance and advice during the progress of this work. They have also to thank Mr. S. G. Plant for assistance in carrying out some of the analytical work.

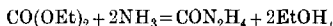
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## LII.—*The Constitution of Carbamides. Part VI. The Mechanism of the Synthesis of Urea from Urethane.*

By EMIL ALPHONSE WERNER.

THE formation of urea from the interaction of ammonia and urethane (ethyl carbamate) has always been considered to afford conclusive evidence in support of the 'carbamide' structure, and is commonly represented by the equation:



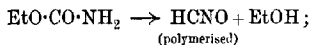
This synthesis of urea is invariably assumed to be analogous to the formation of acetamide from ethyl acetate, urethane being merely recognised as the normal intermediate product.

As a matter of fact, it is nothing of the kind.

When the true mechanism of the change is brought to light, it is seen to be nothing more than a modification of Wöhler's synthesis, namely, the formation of urea from the union of ammonia and cyanic acid in the keto-form.

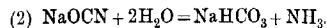
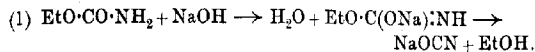
### *Properties of Urethane, and the Conditions under which Urea is formed from the Ester.*

The vapour density of urethane (b. p.  $182^\circ$ ) at  $202.8^\circ$  (b. p. of *m*-cresol) was found to be 43.22, whilst theory requires 44.5; on the other hand, when the ester was boiled under reflux, it was gradually dissociated in accordance with the equation



thus, after two hours, 16 per cent. of the theoretical yield of cyanuric acid was obtained.

The decomposition of the ester by alkali in aqueous solution was found to proceed on the same lines: the change is not a direct hydrolysis, as commonly stated in the literature, and may be represented thus:

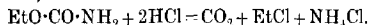


The following results were obtained when urethane and sodium hydroxide (both in *N*/5-solution) were heated at 100°:

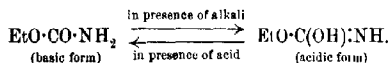
Time in minutes.	Urethane decomposed, per cent.	Sodium cyanate formed, per cent.	Sodium carbonate formed, per cent.
5	50.9	32.9	18.0
15	62.5	37.25	25.25
30	63.95	29.70	34.25
60	66.80	28.80	38.0
90	71.0	17.0	54.0

At 15°, after three days, 18 per cent. of urethane was decomposed, with the formation of 5.5 per cent. of sodium cyanate and 12.5 per cent. of sodium carbonate. The change was therefore independent of dissociation of the ester (compare decomposition of urea, this vol., p. 88).

When urethane was heated in a current of hydrogen chloride, it was decomposed, thus:

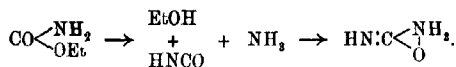


This decomposition of urethane in two different directions may be represented thus:



Since urea is formed from the hydrolysis of cyanic acid, thus,  
 $2\text{HCNO} + \text{H}_2\text{O} = \text{CON}_2\text{H}_4 + \text{CO}_2$

(this vol., p. 95), it is necessary to reach the temperature of the dissociation of urethane in solution in order to obtain urea from it; thus, when the ester was heated in aqueous solution in a sealed tube for two hours at 130°, 5.94 per cent. of the theoretical yield of urea was obtained; after six hours, the yield was 16.62 per cent. (Expts. II and III). Whilst the presence of ammonia would obviously promote the change, the origin of urea in this synthesis is clearly revealed by these results, and is properly represented thus:





A comparative study of the formation of urethane and ammonia from the interaction of urea and ethyl alcohol (a change which is also regarded from a false point of view) has brought to light evidence in support of the above explanations; thus, when a 5*N*-alcoholic solution of urea was heated for two hours at 150°, 41.66 per cent. of the theoretical yield of urethane was formed, as against 33.3 per cent. yield of urea from the interaction of urethane and ammonia under similar conditions (Expts. V and VI).

The greater facility with which urea dissociates explains the higher result in the former case, which otherwise appears abnormal, since the formation of an amide from an ester and ammonia takes place with ease, as compared with the reverse reaction.

Urea is a relatively stable substance, and if it has the 'carbamide' constitution, the question may be asked why it is not formed from ethyl carbonate (or carbamate) with the same ease as undoubted diamides are formed from esters and ammonia; for example, no urea was produced after urethane had remained in contact with a considerable excess of ammonia solution for ten months at the ordinary temperature.

It has been generally accepted as an axiom that the system  $\text{:C(OH)}_2$  cannot form part of a stable molecule; the author now ventures to maintain that the evidence all round is no less convincing as regards the system  $\text{:C(NH}_2)_2$ , and herein lies the true answer to the question just stated. Urea, thiourea, and guanidine are the only known stable substances that have been assumed to contain this system, and in the case of thiourea it is well known that when the thiocarbamic esters  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{OEt}$  and  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SEt}$  respectively are heated with ammonia in alcoholic solution, ammonium thiocyanate is formed. Since the reaction is effected below the temperature at which this salt dissociates (a necessary preliminary for the formation of the isomeride), no thiourea is produced, a fact for which no explanation can be offered when the erroneous 'thiocarbamide' structure is assumed.

As regards guanidine (free base), its constitution has yet to be proved (compare Krall, T., 1915, 107, 1398).

#### EXPERIMENTAL.

The results of the decomposition of urethane by sodium hydroxide in aqueous solution were obtained as follows. A mixture of 0.89 gram of urethane, 10 c.c. of *N*-sodium hydroxide, and 40 c.c. of distilled water was heated to the boiling point under reflux for the stated periods. After the solution had been rapidly cooled,

the 'carbonate' was precipitated by barium nitrate and barium hydroxide; the filtrate, after careful neutralisation with dilute nitric acid, was precipitated with  $N/10$ -silver nitrate, the excess of which was titrated by Volhard's method. Each experiment was made in duplicate.

The results were calculated on the basis:

0.89 Gram of urethane  $\rightarrow$   $\text{BaCO}_3 = 20$  c.c.  $N\text{-HCl}$ .

$\text{NaOCN} = 100$  c.c.  $N/10\text{-AgNO}_3$ .

*Example.*—After one hour,  $\text{BaCO}_3$  precipitated required for neutralisation 7.6 c.c.  $N\text{-HCl}$ , = 38.0 per cent. of the theoretical;  $\text{NaOCN}$  formed required for precipitation 28.8 c.c.  $N/10\text{-AgNO}_3$ , = 28.8 per cent. of the theoretical.

#### *Decomposition of Urethane by Hydrochloric Acid.*

*Expt. I.*—Twenty grams of urethane were heated to  $150\text{--}160^\circ$  in a distillation flask, while hydrogen chloride was passed through the liquid; after a short time crystals began to separate, and the heating was maintained for half an hour. The gas which was evolved (1) burned with a green flame (ethyl chloride), and (2) gave a copious precipitate with excess of barium hydroxide solution (carbon dioxide). The product was treated with ether to remove all unchanged urethane, and the residue, which was readily and completely soluble in cold water, contained  $\text{Cl} = 66.24$  ( $\text{NH}_4\text{Cl}$  requires  $\text{Cl} = 66.35$  per cent.), and gave no reaction for cyanuric acid.

The evolved gas, when collected over warm water, was reduced to almost half its volume after treatment with sodium hydroxide, and the residual gas burnt more freely than before with a green flame. The decomposition was therefore in accordance with the equation given.

#### *Formation of Urea when Urethane was Heated with Water.*

*Expt. II.*—2.5 Grams of urethane and 7.5 c.c. of water were heated in a sealed tube for two hours at  $130^\circ$ . After evaporation of the solution to dryness at  $100^\circ$ , the residue was extracted with ether, when there remained 0.05 gram, which was proved to be urea by the urease test and other reactions.

*Expt. III.*—As before, but the heating was maintained for six hours. Half of the final residue gave, when decomposed by

alkaline sodium hypobromite, 24.28 c.c.  $N_2$  at *N.T.P.*, equal to 0.14 gram of urea, or 16.62 per cent. of the theoretical. Urea nitrate was readily prepared for identification from the remainder.

*Formation of Ethyl Allophanate from Urethane.*

*Expt. IV.*—A solution of 5 grams of urethane in 20 c.c. of alcohol was heated in a sealed tube for three hours at  $150^\circ$ . After evaporation of the alcohol, the residue was extracted with ether, and the insoluble product (0.065 gram) crystallised from hot water in colourless needles melting at  $191^\circ$ , which was the melting point of a specimen of ethyl allophanate used for comparison. When heated with barium hydroxide solution, a copious precipitate of barium carbonate was formed after a few moments, a reaction characteristic of the ester. Whilst the yield was small, the result proves that dissociation of urethane must have taken place.

*Quantitative Comparison of (a) Interaction of Urea and Alcohol,  
(b) Interaction of Urethane and Ammonia.*

*Expt. V.*—A solution of 3 grams of urea in 10 c.c. of alcohol (urea=5*N*) was heated in a sealed tube for two hours at  $150^\circ$ ; from the product, after evaporation of the alcohol and extraction with ether, 1.75 grams of urea were recovered, whilst 1.85 grams of urethane were obtained from the ethereal extract. As 3 grams of urea are equivalent to 4.45 grams of urethane, the yield of the latter was 41.6 per cent. of the theoretical.

*Expt. VI.*—A solution of 4.45 grams of urethane in 10 c.c. of alcohol (urethane=5*N*) which contained 0.85 gram of ammonia was heated as in the last experiment. One gram of urea was obtained after extraction of the residue with ether. Hence the yield was equal to 33.3 per cent. of the theoretical.

A determination of the vapour density of urethane by V. Meyer's method at  $202.8^\circ$  gave the following result: 0.0763 gram gave 21.2 c.c. at  $14.5^\circ$  and 741.45 mm. (corrected), whence *V.D.* = 43.22. Hence there was no dissociation under this condition.

*Summary.*

(1) Urethane is not directly hydrolysed when heated with sodium hydroxide in aqueous solution, as commonly stated; alkali cyanate is first formed, and then hydrolysed.

(2) The formation of urea when urethane (or ethyl carbonate) is heated in solution with ammonia is solely dependent on the dissociation of urethane, and is no more than a repetition of Wöhler's synthesis in a modified form.

(3) A comparison of the reaction with the formation of urethane from urea and alcohol supplies evidence which is opposed to the 'carbamide' formula.

(4) Attention is directed to a rational inference from the facts, namely, that the system  $\text{C}(\text{NH}_2)_2$  cannot form part of a stable molecule.

The author desires to express his thanks to Miss M. Coade, B.Sc., for her assistance in conducting part of the experimental work.

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TRINITY COLLEGE, DUBLIN.

[Received, June 18th, 1918.]



## Organic Chemistry.

**The Oxidation Products of Paraffin.** MAXIMILIAN BERGMANN (*Zeitsch. angew. Chem.*, 1918, **31**, 69—70).—White, refined paraffin wax of Galician origin, m. p.  $52^{\circ}$ , was oxidised by blowing a fairly rapid current of air through it at  $130$ — $135^{\circ}$  for fifteen to eighteen days. The soft brown product of the oxidation had an acid value of 132 and gave strongly frothing soap solutions with alkali hydroxides. On distilling the crude mass, decomposition set in at about  $300^{\circ}$ , with formation of formic, acetic, and *n*-butyric acids. The separation of the fatty acids from the neutral substances was therefore effected by forming the barium soaps and extracting the dried precipitate with ether. The isolated fatty acids had an acid value of 200 and were fractionated by distillation under 100 mm. pressure; about one-half distilled between  $230^{\circ}$  and  $270^{\circ}$  and one-third between  $270^{\circ}$  and  $310^{\circ}$ . The latter fraction showed an iodine value of 4; it was converted into the lithium soap, which was dried and extracted with ether and light petroleum, to separate the last traces of unsaponifiable matter. The liberated fatty acid was converted into the ethyl ester, m. p.  $55^{\circ}$ , after recrystallisation from alcohol. The purified acid had m. p.  $80.1^{\circ}$ . It was thus characterised as *lignoceric acid*, and proved to be identical with the lignoceric acid prepared from earth-nut oil. The fraction boiling between  $230^{\circ}$  and  $270^{\circ}$  had an iodine value of 5; by extraction of its lithium soap, a neutral substance was extracted crystallising from methyl alcohol in leaflets, m. p.  $48^{\circ}$ . The liberated fatty acids were separated by crystallisation from acetic acid into two substances: one crystallising in shining needles, m. p.  $53.7^{\circ}$ , acid value 299.4, corresponding with the formula  $C_{11}H_{22}O_2$ , which gave strongly frothing soap solutions with alkali hydroxides; and the other, separated from the mother liquors by precipitation as the lithium soap, which had m. p.  $210$ — $212^{\circ}$ , having a composition corresponding with  $C_{16}H_{32}O_2$ , m. p.  $38.4^{\circ}$ , and acid value 217.05. The latter acid might be an *isopalmitic acid*. J. F. B.

**Solubility of Hydrocarbons (Paraffin, Aromatic, Naphthene and Olefine) in Liquid Sulphur Dioxide.** R. J. MOORE, J. C. MORELL, and G. EGLOFF (*Met. and Chem. Eng.*, 1918, **18**, 396—402).—The solubility of individual hydrocarbons, of binary mixtures, and of a ternary mixture, of paraffins, aromatic hydrocarbons, and naphthenes has been studied. Solubilities were determined by bringing the liquid sulphur dioxide and the hydrocarbons together in a burette immersed in a freezing mixture of ice, salt, and calcium chloride at temperatures down to  $-18^{\circ}$ . Benzene, toluene, xylene, mesitylene, and olefines were miscible with the solvent in all proportions. Paraffins up to decane were practically insoluble. Naphthenes showed a solubility limited

at  $-18^{\circ}$ , which was more pronounced at  $-4.5^{\circ}$ . There is evidence of the formation of a molecular compound with the solvent. The separation of the mixed hydrocarbons of different types by liquid sulphur dioxide is limited by the partition of the hydrocarbons between the two phases, but by attention to the relative proportions, some approximation to a quantitative separation is possible, generally where the constituent to be extracted is in small proportion. Aromatic hydrocarbons and olefines, together or separate, can be separated from paraffins and naphthenes. Naphthenes can be separated from paraffins. Over methods of sulphonation and nitration, this method has the advantage of permitting recovery of both hydrocarbon and solvent and also of avoiding the production of undesirable by-products.

H. J. H.

**Action of Concentrated Sulphuric Acid on Olefines, with Particular Reference to the Refining of Petroleum Distillates.** BENJAMIN T. BROOKS and IRWIN HUMPHREY (*J. Amer. Chem. Soc.*, 1918, **40**, 822—856).—The data at present available as to the behaviour of various olefines with sulphuric acid are scanty and somewhat conflicting, and as a preliminary to an investigation of the action of sulphuric acid on olefines as applied in the refinery of petroleum distillates, the authors have examined the effect of sulphuric acid on synthetic unsaturated hydrocarbons of definite purity and known constitution.

The chief results of the action of sulphuric acid on olefines are polymerisation and the formation of secondary and tertiary alcohols and of alkyl hydrogen and dialkyl sulphates. Contrary to the general assumption in the petroleum industry, no mono-olefine hydrocarbon was found to yield a "tar" when treated with the acid at  $15^{\circ}$ . In the aliphatic series, the tendency to form alkyl sulphates and alcohols decreases with increasing molecular weight above the amylenes and hexenes, at which a maximum is observed (compare Michael and Brunel, A., 1909, i, 197; 1912, i, 821). The introduction of strongly electronegative groups into ethylene causes a decrease in the reactivity towards sulphuric acid, as is demonstrated by the relative inertness of fumaric and cinnamic acids and of dichloroethylene towards the acid, whilst, inversely, *γ*-dimethyl- $\Delta^2$ -butylene, in which each of the hydrogen atoms is replaced by the electro-positive methyl radicle, is more reactive than the isomeric  $\alpha$ -hexene; a similar consideration also explains the greater reactivity of amylene, butylene, and propylene as compared with ethylene. This point of view, however, fails to explain the relative stability of the olefines of still higher molecular weight, nor does it appear to throw much light on the difference between the behaviour of  $\gamma$ -ethyl- $\Delta^2$ -pentene, which yields 72% of the alcohol and 12% of polymerides and of the structurally similar  $\beta$ -methyl- $\Delta^2$ -undecene, which gives 97% polymerides and a trace of alcohol, or on the fact that vinylacetic acid yields crotonic acid, whereas the isomeric  $\alpha$ -methylacrylic acid gives a polymerisation product; styrene, cinnamyl alcohol, eugenol, *isoeugenol*, and saffrole also

undergo vigorous polymerisation to hard, resinous substances. With increasing molecular weight, the tendency towards polymerisation develops, and duodecene is found to undergo almost quantitative conversion into a dipolymeride; the polymerides generally are open-chain hydrocarbons still containing at least one double bond, and are naturally much more stable than the parent olefines towards sulphuric acid; the result of this is that when petroleum is refined with sulphuric acid, the viscous polymerides are not found in the used acid, but remain to a large extent in the layer of refined oil. The common assumption that the more viscous petroleum oils, for example, of the lubricating oil type, consist exclusively of naphthenes and polynaphthenes is therefore not above suspicion, and the presence of a considerable percentage of polymerised olefines is probable, not only from the fact that the oils have been treated with sulphuric acid, but from the definite iodine value of such oils.

When the simpler alkylenes are dissolved in cold 85% sulphuric acid at below 15°, clear amber-coloured solutions are obtained which on treatment with ice give an immediate oily precipitate consisting mainly of the corresponding alcohol, whilst the aqueous acid solution, containing a considerable proportion of the original hydrocarbon as the alkyl hydrogen sulphate, fails to yield any appreciable further deposit of oil even during several days; the alkyl hydrogen sulphates, therefore, are not readily hydrolysed under such conditions; from these results and the fact that pure sulphuric acid alone does not convert hexenes into the alcohols, it is probable that the formation of alcohols by the action of diluted sulphuric acid on alkylenes may be independent of any intermediate occurrence of sulphuric esters of the known type and may be attributed to the intermediate formation of an easily hydrolysable orthosulphate analogous to sulphuric acid monohydrate,  $H_4SO_5$ , or of an easily hydratable additive compound of the olefine with sulphuric acid corresponding with the zinc chloride or aluminium chloride additive compounds (compare Gangloff and Henderson, A., 1916, i, 593; 1917, i, 533).

In the course of the investigation, the following olefinic hydrocarbons were examined in a high degree of purity:  $\beta$ -methyl- $\Delta^1$ -butylene, b. p. 33—35°;  $\beta$ -methyl- $\Delta^2$ -pentene, b. p. 64—66°;  $\Delta^1$ -n-hexene, b. p. 60·5—61·5° (earlier descriptions are inaccurate), the constitution of which is demonstrated by its conversion through the chlorohydrin into the corresponding glycol;  $\epsilon$ -methyl- $\Delta^2$ -hexene (isohexene),  $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$ , b. p. 85—86°,  $D_{20}^{25} 0\cdot7160$ ;  $\Delta^1$ -n-heptene, b. p. 93—95°,  $D_{20}^{25} 0\cdot7020$ , which combines with benzenesulphonic acid at the ordinary temperature, yielding an undistillable heptyl benzenesulphonate,  $D_{20}^{25} 0\cdot979$ ;  $\gamma$ -ethyl- $\Delta^2$ -pentene, b. p. 97—98°;  $\beta\gamma$ -dimethyl- $\Delta^2$ -butene (tetramethylethylene), b. p. 73—74°,  $D_{20}^{25} 0\cdot7075$ ;  $\Delta^2$ -octene, b. p. 122—124°,  $D_{20}^{25} 0\cdot7240$  (dipolymeride, b. p. 195—230°), although it is not certain that this may not in reality be the  $\Delta^2$ -isomeride;  $\xi$ -methyl- $\Delta^2$ -heptene (isooctene),  $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH : CH_2$ , b. p.



111—112°,  $D_4^{20}$  0.7125,  $n_D^{20}$  1.3986 (*dipolymeride*, b. p. 112—114°, 16 mm.,  $D_4^{20}$  0.798);  $\beta$ -methyl- $\Delta^8$ -undecene,  $\text{CMe}_2\text{CH}=\text{C}_8\text{H}_{17}$ , b. p. 210—211.5°/752 mm.,  $D_4^{20}$  0.7590,  $n_D^{20}$  1.4270. For the synthetic production of  $\Delta$ -ethylenic hydrocarbons, the interaction of allyl bromide and a magnesium alkyl bromide was found convenient; the formation of unsaturated hydrocarbons by the action of heat on the higher alcohols is found to be greatly facilitated by the addition of a little iodine. In the preparation of  $\zeta$ -methyl- $\Delta$ -heptene by the former method, using magnesium *iso*amyl bromide and allyl bromide, a *decane*, b. p. 156.5—157.5°,  $n_D^{20}$  1.4006,  $D_4^{20}$  0.7270, probably of the constitution  $\text{C}_2\text{H}_4(\text{CH}_2\text{CHMe})_2$ , was obtained as a by-product. D. F. T.

**Preparation of Glycols.** CHEMICAL DEVELOPMENT CO. (U.S. Pat. 1259757).—A mixture of olefine dichlorides prepared from oil-gas is converted into the corresponding glycols (ethylene, propylene, and butylene glycols) by heating with water and calcium carbonate under pressure. A. S.

**Preparation of Glycols and Glycol Derivatives.** CHEMICAL DEVELOPMENT CO. (U.S. Pat. 1259758).—A mixture of olefine dihaloids is heated under pressure with the calcium salt of a weak acid, for example, calcium acetate. (See also preceding abstract.) A. S.

**Lecithin. II. Preparation of Pure Lecithin; Composition and Stability of Lecithin-Cadmium Chloride.** P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1918, **34**, 175—186. Compare this vol., i, 98).—Pure lecithin may be obtained from egg yolk by extracting with acetone and alcohol, and then redissolving the concentrated extract several times in dry acetone, which effects a separation from lipoids insoluble in acetone. The oil is then extracted with a large volume of hot alcohol, the alcoholic extract cooled to 0°, the solution decanted from the egg-fat, concentrated, and the lipid mixture precipitated with cadmium chloride. The lecithin-cadmium chloride is recrystallised from a mixture of ethyl acetate and 80% alcohol until free from amino-nitrogen (kephalin), and is then decomposed by ammonium carbonate according to Bergell's method (A., 1900, i, 621). The resulting lecithin does not contain any amino-nitrogen. H. W. B.

**Preparation of Acetic Acid from Acetaldehyde.** H. DREYFUS (Brit. Pat. 108459. Compare this vol., i, 251).—The oxidation of acetaldehyde to acetic acid by means of air or oxygen, either in presence or absence of contact substances, is most complete if effected at 150—250°, preferably 150—200°. Copper (clippings, gauze, powder) is a more efficient catalyst than platinum. Chromium compounds are also very efficient, and other suitable catalysts are copper oxide, iron, uranium oxide, vanadium oxide, and cerium oxide. A. S.

**Preparation of Acetic Anhydride and Polymerised or Non-polymerised Acetaldehyde.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 110906).—Ethylidene diacetate is decomposed almost quantitatively into acetic anhydride and paraldehyde by heating it in a vacuum with an acid or acid salt as catalyst, for example, with 2% of sulphuric acid (D 1'84) at 70–80°/100 mm.

A. S.

**The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol.** MARY EVELYN LAING (T., 1918, 113, 435–444).—Measurements have been made of the changes in the boiling point of ethyl alcohol which are produced by the addition of gradually increasing quantities of potassium oleate. The molecular weight calculated from the results is independent of the concentration and slightly less than that corresponding with the formula. In moist alcohol similar results were obtained.

From the measured values of the electrical conductivity at 40° and 60°, it is inferred that the ionisation increases from about 3% in 1*N*. to about 30% in 0.03*N*-solution.

The conductivity of solutions of oleic acid in ethyl alcohol has also been measured at 60° over a wide range of concentration. The degree of ionisation is very small, and the results afford evidence that the ionisation varies with dilution in accordance with the requirements of the law of mass action.

The conductivity of potassium oleate in alcohol is diminished by the addition of oleic acid. This suggests the formation of a complex compound, and evidence in support of this hypothesis is afforded by boiling point observations on solutions containing mixtures of the salt and acid.

The observations on potassium oleate agree with those previously made by Krafft on the salts of other fatty acids and show that these substances behave as normal electrolytes in alcohol, although in aqueous solution they afford examples of colloidal electrolytes.

H. M. D.

**Preparation of a Crystalline Ester of the Di-iodide of Ricinastearolic Acid.** J. D. RIEDEL (D.R.-P., 303052, 1914; from *Chem. Zentr.*, 1918, i, 498).—Ethyl ricinastearolate di-iodide, colourless needles, m. p. 31°, can be obtained by esterifying the di-iodide of ricinastearolic acid or by the addition of iodine to ethyl ricinastearolate.

D. F. T.

**Ethyl Thioacetoacetate [Ethyl Acetoacetate Sulphide], Ethyl  $\alpha$ -Chloroacetoacetate, and a New Formation of Oxalic Acid.** FR. VON KONEK-NORWALL (*Ber.*, 1918, 51, 391–398).—When antipyrine is treated with sulphur chlorides, it yields a mono- and di-sulphide (A., 1911, i, 505), but the parent ethyl acetoacetate only forms a monosulphide,  $S(CHAc\cdot CO_2Et)_2$  (A., 1885, 1200). With the hope of obtaining a disulphide, some pure ethyl  $\alpha$ -chloroacetoacetate was purchased about six years ago to

be treated with sulphur, but it was recently found that the specimens had gradually deposited crystals of oxalic acid dihydrate.

J. C. W.

**Photochemical Reactions in Aqueous Solution. II.** ALFRED BENRATH (*J. pr. Chem.*, 1917, [ii], **96**, 190—201. Compare A., 1912, ii, 881; 1911, ii, 681).—When mixed with iron alum in aqueous solution in a sealed glass tube exposed to sunlight, tartaric acid undergoes photochemical oxidation with formation of dihydroxytartaric acid, which is not isolable, but rapidly decomposes in part into glyoxalcarboxylic acid,  $\text{CHO}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , and carbon dioxide (compare Ciamician and Silber, A., 1913, ii, 545; Seekamp, A., 1894, i, 323); the formation of this acid is proved by its isolation as its di-phenylhydrazone and by the relative proportion of the reagents which participate in the change. Part of the dihydroxytartaric acid, however, undergoes further oxidation to carbon dioxide, probably by way of mesoxalic acid, and carbon dioxide is also formed as the final product in the further oxidation of the glyoxalcarboxylic acid, probably through tartronic acid and mesoxalic acid; small quantities of glyoxal, glyoxylic acid, and formaldehyde can also be detected, but these are regarded as by-products, the first being produced by the partial elimination of carbon dioxide from glyoxalcarboxylic acid, whilst the last two form minor successive oxidation products of mesoxalic acid. The correctness of these views is confirmed by photochemical experiments with the postulated intermediate products.

Citric acid in aqueous solution, with the addition of iron alum and a little sulphuric acid, becomes oxidised in sunlight during the course of a few days with formation of carbon dioxide, acetone, and a little formaldehyde. In a similar oxidation of glycollic acid, formaldehyde and glyoxylic acid can be detected, whilst malic acid is relatively resistant, and the only identified products were acetaldehyde and formaldehyde.

When a mixture of formic acid with ethyl alcohol, or acetic acid with methyl alcohol, in a sealed tube is exposed to light for twelve months, the resulting liquid can be shown to contain the corresponding ester, together with formaldehyde and acetaldehyde in addition to unchanged ingredients, whilst with acetic acid and ethyl alcohol only ethyl acetate and acetaldehyde are formed; the conclusion is drawn that the resulting ester undergoes partial decomposition into the two aldehydes. In a similar manner, a mixture of formic and malic acids produces carbon dioxide, formaldehyde, and acetaldehyde, and the same substances are formed in the interaction of oxalic acid and acetone; a mixture of formic acid and citric acid yields carbon dioxide, formaldehyde, and acetone, and a mixture of formic acid and acetone gives rise to formaldehyde.

D. F. T.

**Formaldehyde in Air.** D. G. J. BOLTEN (*Pharm. Weekblad*, 1918, **55**, 60—61).—The evolution of formaldehyde vapour from formalin for disinfecting purposes can be brought about by the action of quicklime. The process has the advantage that there

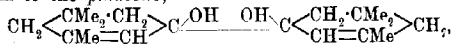
is no oxidation of the formaldehyde. In the permanganate method, 2% of the formaldehyde is lost through oxidation. A. J. W.

**Preparation of Dialdehydesulphoxylic Acids.** ARTHUR BINZ (D.R.-P., 303478, 1916; from *Chem. Zentr.*, 1918, i, 498).—*Di*formaldehydesulphoxylic acid,  $S(O\cdot CH_2\cdot OH)_2$ , can be obtained from a formaldehydesulphoxylate, formaldehyde solution, and alcoholic hydrogen chloride; similarly, *dibenzaldehydesulphoxylic acid* is obtainable from benzaldehydesulphoxylate. The analogous *formaldehydebenzaldehydesulphoxylic acid*,  $OH\cdot CH_2\cdot O\cdot S\cdot O\cdot CHPh\cdot OH$ , reacts with *p*-toluidine, yielding the substance  $C_6H_4Me\cdot NH\cdot CH_2\cdot O\cdot S\cdot O\cdot CHPh\cdot OH$ . D. F. T.

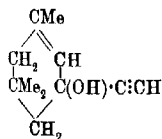
### Action of Sodium Acetylide on Aldehydes and Ketones.

K. HESS and H. MUNDERLOH (*Ber.*, 1918, 51, 377—384).—Primary, secondary, and tertiary alcohols of the acetylene series have been prepared by the action of sodium phenylacetylide,  $CPh\cdot CNa$ , on formaldehyde, other aldehydes and ketones, respectively (compare Nef, 1899, and Moureu, 1901—1902). The behaviour of unsubstituted sodium acetylide,  $CH\cdot CNa$ , has therefore been examined. This is found to react in the above manner to a very minor extent. Generally speaking, most of the acetylene escapes as gas, the sodium uniting with the carbonylic compound and inducing polymerisation and intermolecular condensations.

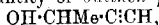
Acetone reacts vigorously, even at  $-15^\circ$ , about 64% of the acetylide decomposing into gas. After decomposing the product with dilute sulphuric acid, extracting with ether, and fractionating the oil thus isolated, the following compounds were obtained: (I.) *γ*-Methylbutinen-*γ*-ol,  $OH\cdot CMe_2\cdot C\cdot CH$ , a volatile, mobile, pungent-smelling oil, b. p.  $102-103^\circ/745$  mm.,  $25^\circ/12$  mm., yield 2.8%; this gives a white precipitate with mercuric chloride which yields trimethylketol, identified by its semicarbazone (Schmidt and Austin, A., 1902, i, 2), on boiling with hydrochloric acid. (II.) Mesityl oxide, sufficient in quantity to identify as its semicarbazone. (III.) Diacetone alcohol, b. p.  $67-68^\circ/19$  mm., yield about 1.3%. (IV.) *iso*Phorone, b. p.  $86-87^\circ/11$  mm., yield 36.9%; this has been identified by its semicarbazone and also reduced by sodium amalgam to the *pinacone*,



m. p.  $162^\circ$ . (V.) "*iso*Phorone-acetylene" (annexed formula), a viscous, pungent oil, b. p.  $115-116^\circ/12$  mm., yield 2.2%.



Reaction with acetaldehyde is still more vigorous. The only recognisable product is a minute quantity of *butinen-γ*-ol,



which is a limpid, lachrymatory oil, b. p.  $105-106^\circ/742$  mm. Benzaldehyde gives as

the chief product benzyl benzoate.

Notes on the preparation of sodium acetylide are given. J. C. W.

**The Influence of Certain Substances on Starch Solutions, and the Action of Amylase of the Saliva.** J. TEMMINCK GROLL (*Arch. néerland. physiol.*, 1918, **2**, 319—336).—Reversible transformations of starch into an erythroamylose, giving a red or violet colour with iodine-potassium iodide solution, take place when starch solutions are treated with methyl, ethyl, or octyl alcohol, ethyl ether, and chloroform in various concentrations. If sodium cholate or saponin is added in addition to these substances, the transformation into erythroamylose becomes irreversible. This action of cholate and saponin is ascribed to a surface-tension effect. The salivary amylase, under the influence of cholate and saponin, acts on starch solutions, producing reducing substances which colour the iodine solution red or brown. After some minutes, however, the starchy substance is reconstituted, the reducing substances disappear, and the solution gives a blue colour with iodine. After a further long period, the starchy substance disappears, and products are produced which do not colour iodine. It is suggested that it is possible, by simply lowering surface tension, to obtain catalytic decomposition of a colloidal substrate (soluble starch).

S. B. S.

**Wood Pulp.** CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1918, **31**, 50—56; 57—60).—A description of the different classes of wood pulp and of its chemical properties. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

**Two Forms of Glycine.** K. GEORGE FALK and KANEMATSU SUGIURA (*J. Biol. Chem.*, 1918, **34**, 29—36. Compare Fischer, A., 1905, i, 863).—Glycine crystallises from water in plates and from dilute alcohol in needles. After drying at 100°, the plate form begins to decompose on heating at 212°, whilst the needle form remains unchanged until a temperature of 220° to 230° is reached. There are also differences in the behaviour of the two forms towards nitrous acid and towards bromine; in one experiment, each molecule of the needle form absorbed 2 atoms of bromine, whilst the plate form absorbed 1 atom. Similar experiments with the corresponding two forms of alanine showed similar although less marked differences. Possible structural formulæ are suggested to account for the observed differences between the two forms of glycine and alanine respectively.

H. W. B.

**Preparation of Formamide.** ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 793—796).—Formamide purified by fractional distillation has m. p. 2·25° (English and Turner, *Trans.*, 1914, 105, 1656, give 2·0—2·2°). [See also *J. Soc. Chem. Ind.*, July.]

D. F. T.

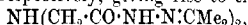
**Rotatory Powers of the Amides of Active  $\alpha$ -Hydroxy-acids.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1918, **40**, 813—817).—The sign of the optical activity of the amides of *d*-gluconic acid, *d*-galactonic acid, *l*-mannonic acid, *d*-gulonic acid, *l*-arabonic acid, *l*-ribonic acid, and *d*-xylonic acid (Weerman, A., 1915, i, 387;

1917, i, 546), as also of the amides of *d*-α-glucosheptonic acid and of *l*-rhammonic acid in aqueous solution, is in agreement with the general rule that the dextrorotatory amides have the α-hydroxyl group below the asymmetric α-carbon atom, whilst with the levorotatory amides it is above, the constitutions being represented by ordinary plane formulæ placed horizontally with the amide group to the right (compare Levene, A., 1916, ii, 3; Levene and Meyer, A., 1916, ii, 545; 1917, i, 631; Hudson, A., 1910, i, 220; 1917, i, 318). This result is in accord with the structure of *d*-tartaric acid as decided by Fischer (A., 1896, i, 525) and with the direction of the optical activity of tartramic acid (Weerman, *loc. cit.*) and of the amides of tartaric acid (Frankland and Slaton, T., 1903, 83, 1354; Frankland and Twiss, T., 1906, 89, 1853). The optical activities of the amide of *l*-malic acid (Walden, A., 1896, i, 139) and of the amide of *d*-glyceric acid (Frankland and Wharton, T., 1901, 79, 266) are also found to obey this rule, and the agreement serves to confirm the structures attributed to these acids (Freudenberg, A., 1914, i, 924). The amide derived from amygdalin mandelic acid has a levorotation, and on this evidence the α-hydroxyl group in this mandelic acid is believed to occupy a position above the asymmetric atom when the structure is formulated in the manner described.

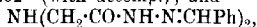
D. F. T.

**Hydrazides and Azides of Organic Acids. XXXIII. The Action of Hydrazine and Nitrous Acid on Di- and Triglycollamic Esters.** THEODOR CURTIUS and OTTO HOFMANN (*J. pr. Chem.*, 1917, [ii], 96, 202—235).—Iminodiacetic acid (diglycollamic acid) can be obtained conveniently by heating chloroacetic acid with the additive compound of zinc chloride and ammonia, esterifying the resulting mixture of acids by heating with alcoholic hydrogen chloride and then separating the ethyl esters of aminoacetic acid, iminodiacetic acid, and nitrilotriacetic acid by distillation under reduced pressure; another very convenient process is based on that of Jongkees (A., 1908, i, 959) for the preparation of iminodiacetonitrile, which by treatment with alcoholic hydrogen chloride can be converted directly into ethyl iminodiacetate (compare Dubsy and Gränacher, *this vol.*, i, 188); if iminodiacetonitrile is suspended in ether and submitted to the action of nitrous fumes, nitrosoiminodiacetonitrile is obtained, m. p. 43° (Bailey and Snyder, A., 1915, i, 389, give m. p. 38°).

Ethyl iminodiacetate, D<sup>16</sup> 1.0851, b. p. 133°/11 mm., reacts with hydrazine hydrate at the ordinary temperature, yielding *iminodiacetic hydrazide*,  $\text{NH}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$ , leaflets or tablets, m. p. 133°, which forms a *trihydrochloride*, a *triacetyl* derivative, m. p. 204—205° (decomp.), and slowly reacts with ketones and aldehydes, giving condensation products; acetone, salicylaldehyde, and benzaldehyde respectively, giving rise to the *compounds*



small rods, m. p. 176°;  $\text{NH}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ , small rods, m. p. 201—202° (with decomp.); and

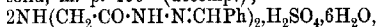


q\*

small rods, m. p. 201—202° (decomp.). If the condensation is allowed to proceed in the presence of mineral acid, the products are the corresponding salts of these substances, and always contain water of crystallisation, thus

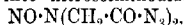


pale yellow solid, m. p. 190° (decomp.);

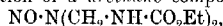


m. p. 173—175°;  $\text{NH}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2, \text{HCl}, 2\text{H}_2\text{O}$ , needles, m. p. 249—250°;  $\text{NH}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2, \text{HNO}_3, 2\text{H}_2\text{O}$ , m. p. 202—203°;  $\text{NH}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2, \text{HNO}_2, 2\text{H}_2\text{O}$ , m. p. indistinct near 135°; it was not found possible to convert the last, by dehydration, into a nitroso-compound.

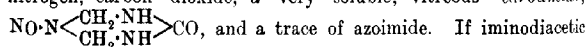
On treatment with nitrous gases, ethyl iminodiglycollate is converted into *ethyl nitrosoiminodiacetate*,  $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , a viscous, yellow oil, b. p. 175°/14 mm., which is also obtainable from ethyl iminodiacetate hydrochloride and sodium nitrite in the presence of water, and from nitrosoiminodiacetonitrile by the action of alcohol and hydrogen chloride. Ethyl nitrosoiminodiacetate reacts with alcoholic ammonia solution, giving nitrosoiminodiacetamide,  $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ , pale yellow tablets, m. p. 153°, and forms a dihydrazide (Curtius, Darapsky, and Müller, A., 1908, i, 145), which is convertible into a *diacetyl* derivative, m. p. 213—214° (decomp.), and readily condenses with acetone, producing a *substance*,  $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_3)_2$ , needles, m. p. 232° (decomp.). When treated in aqueous solution with sodium nitrite and the calculated quantity of hydrochloric acid, the nitrosohydrazide undergoes conversion into nitrosoiminodiacetic azide,



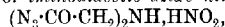
a yellow oil which reacts with hydrazine hydrate, re-forming the hydrazide, and on treatment with aniline gives *nitrosoiminodiacetanilide*,  $\text{NO}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})_2$ , colourless needles, m. p. 224—225°. Boiling alcohol decomposes the azide in the normal manner, with formation of a *urethane* compound,



colourless crystals, m. p. 70°, which reacts readily with cold hydrochloric acid, giving an effervescence of carbon dioxide and producing anhydroformaldehyde urethane,  $\text{C}_8\text{H}_{14}\text{O}_4\text{N}_2$  (Conrad and Hock, A., 1903, i, 607), but can be completely hydrolysed to ammonia, formaldehyde, carbon dioxide, and alcohol by dilute hydrochloric acid in a sealed tube or by barium hydroxide solution; hot water causes a slow decomposition of the azide into nitrogen, carbon dioxide, a very soluble, vitreous *carbamide*,

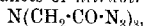


hydrazide trihydrochloride is treated in the presence of a little water with sodium nitrite, liberation of nitrogen occurs, together with the formation of *iminodiacetic azide nitrite*,



colourless needles, accompanied by the yellow nitroso-azide already mentioned; like the latter, the nitrite readily reacts with aniline, giving the nitrosoanilide.

Ethyl nitrilotriacetate (ethyl triglycollamate), prepared from the reaction product of chloroacetic acid and the additive compound of zinc chloride and ammonia or from nitrilotriacetonitrile, reacts only slowly with hydrazine hydrate, the resulting hygroscopic, vitreous *trihydrazide*,  $N(CH_2 \cdot CO \cdot NH \cdot NH_2)_3$  (*tetrahydrochloride*), being converted by acetone and benzaldehyde into *condensation products*,  $N(CH_2 \cdot CO \cdot NH \cdot N \cdot CMe_2)_3$ , small, colourless rods, m. p.  $205^\circ$  (decomp.), and  $N(CH_2 \cdot CO \cdot NH \cdot N \cdot ClPh)_3$ , an amorphous powder, m. p.  $206^\circ$  (decomp.), respectively; the former can be converted into the latter by treatment with benzaldehyde. The addition of sodium nitrite to an aqueous solution of the nitrilotriacetic hydrazide hydrochloride causes immediate effervescence and formation of explosive leaflets of *nitrilotriacetic azide*,



together with a sparingly soluble substance, probably a hydrazide. D. F. T.

**Preparation of Trialkylethanolarsonium Hydroxides and their Salts.** CHEMISCHE WERKE GRENZACH (D.R.-P., 303032, 1916; from *Chem. Zentr.*, 1918, i, 498).—By hydrolysis of halogenethyl-trialkylarsonium haloids with water at higher temperatures, it is possible to produce arsonium compounds analogous to choline, and having valuable therapeutic properties. Trimethylarsine and ethylene bromide react at  $100$ – $105^\circ$ , yielding *trimethyl- $\beta$ -bromoethylarsonium bromide*, prismatic tablets, m. p.  $239^\circ$  (corresponding *picrate*, m. p.  $189^\circ$ ), which is converted by water at  $180^\circ$  into *trimethylathanolarsonium bromide*,  $C_2H_5OBrAs$ , deliquescent prisms, m. p.  $219^\circ$ . *Triethyl- $\beta$ -bromoethylarsonium bromide*, m. p.  $225^\circ$ , obtained from triethylarsine and ethylene bromide, on treatment with water at  $180^\circ$ , yields *triethylathanolarsonium bromide*, needles. D. F. T.

**Preparation of Benzenesulphonic Acid.** J. W. AYLSWORTH (U.S. Pat. 1260852).—Excess of benzene is heated with sulphuric acid in a closed vessel, at a temperature increasing progressively during several hours from  $70^\circ$  to  $120^\circ$ . The mass is then cooled below  $70^\circ$ , and, while stirring, a quantity of sulphur trioxide sufficient to combine with the water present is added, and the whole is again heated as before, the series of operations being repeated as many times as is necessary. A. S.

**Preparation of *p*-Cymenesulphonic Acid.** RHEINISCHE CAMPHER-FABRIK (D.R.-P., 303095, 1916; from *Chem. Zentr.*, 1918, i, 498).—2-Bromo-*p*-cymene-3-sulphonic acid can be conveniently reduced by heating with ordinary or activated zinc and sodium hydroxide solution. D. F. T.

**Spinacene and some of its Derivatives.** A. CHASTON CHAPMAN (T., 1918, 113, 458–466. Compare *ibid.*, 1917, 111, 56).—The author now assigns to spinacene the formula  $C_{29}H_{48}$ . It has b. p.  $260^\circ$  (corr.)/9 mm.,  $D_4^{20}$  0.8610,  $n_D^{20}$  1.4956, iodine value



(Wij's method) 367.9. The hexahydrochloride has m. p. 126°, and when heated at 190°, under reduced pressure, loses its hydrogen chloride, and gives a *hydrocarbon* differing from spinacene in being less unsaturated. Dry hydrogen bromide, when passed into a cooled solution of spinacene in dry ether, gives a *hexahydrobromide*,  $C_{30}H_{48} \cdot 6HBr$ , m. p. 132°. When warmed with dilute nitric acid (1:1), spinacene gives at least two products. When distilled over sodium at a pressure of 45 mm., spinacene is decomposed somewhat, four fractions being obtained: (1)-b. p. 84–88°/45 mm.; (2) b. p. 155–175°/45 mm.; (3) b. p. 220–275°/45 mm.; (4) b. p. 295–298°/45 mm., and a colourless, viscous residue. Fraction (1), when purified by steam distillation, had b. p. 60°/20 mm., and was apparently a *cyclodihydroterpene*, which may prove to be identical with *cyclodihydromyrcene* or with *cyclolinaloolene*. W. G.

**A New Dehydrogenation Method. Synthesis of Decacyclene, Fluorocyclene, and Chlorene, a Green Hydrocarbon.**

K. DZIEWOŃSKI and S. SUKNAROWSKI (*Ber.*, 1918, 51, 457–465).—It has already been shown that acenaphthylene yields decacyclene when heated at 280–290° (*A.*, 1914, i, 826). In the hope of obtaining larger quantities of the latter hydrocarbon, other condensations in this field have been investigated, and it is now shown that both compounds can be prepared most conveniently by heating acenaphthene with lead oxide in a sealed tube. A third hydrocarbon is also formed in small quantities by this method. Being deep green in colour, it is designated *chlorene*.

For the preparation of decacyclene,  $C_{30}H_{18}$ , acenaphthene (10 grams) is heated with lead oxide (3.5) for three to four hours at 370–380° in a Carius tube. Unchanged acenaphthene is removed by boiling the product with alcohol, greenish-brown impurities by means of cold benzene, most of the fluorocyclene by boiling benzene, and most of the decacyclene by boiling cumene. The yield of the latter is 30–35%. For the preparation of fluorocyclene in a yield of as much as 25%, acenaphthene is heated with three times its weight of lead oxide for twenty hours at 330–340°, the tube being cooled to 110° every few hours and opened to let the steam escape. Fluorocyclene,  $C_{18}H_{10}$ , crystallises in small, orange-yellow rhombohedra belonging to the triclinic system, m. p. 396–397°.

The third hydrocarbon is found among the greenish-brown "impurities" and is formed in largest amount by heating acenaphthene with three times its weight of lead oxide for five to eight hours at 350°. It is isolated by protracted treatment with benzene and light petroleum in the cold, being more soluble in the mixture than certain yellow by-products. *Chlorene*,  $C_{18}H_{10}$ , crystallises in small, dark green scales, which shrink at about 265°, but are not molten at 300°. Dilute solutions are pure deep green in colour, but become brownish-red on exposure to sunlight. Concentrated solutions appear purple-red by a bright transmitted light. The spectrum shows the following absorption bands:  $\lambda = 648\text{--}600 \mu$ , very dark

and well defined; 550—546, much paler; 490 to the end of the visible violet, a faint band. J. C. W.

**The Replacement in Amides of an Alkylanilino group by an Aniline group by Heating with Aniline Hydrochloride.**

G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 983—985).—When 2 molecules of aniline are heated at 190° with 1 molecule of phenylmethylcarbonyl chloride, *s*-diphenylcarbamide is obtained. This substance is also formed when methyl carbanilide is heated with aniline hydrochloride. Replacement of the alkylaniline group is also found to occur when dimethyl- and diethyl-carbanilides are heated with aniline hydrochloride, and in similar circumstances, dimethyloxanilide gives oxanilide.

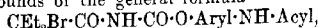
The replacement does not take place at lower temperatures, for when an ethereal solution of 1 molecule of phenylmethylcarbonyl chloride is heated with 2 molecules of aniline, the product obtained is methylcarbanilide. H. M. D.

**Production of Aryl Sulphites.**

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 303033, 1916; from *Chem. Zentr.*, 1918, i, 499).—Aromatic sulphites are obtainable by treating aromatic hydroxyl compounds with thionyl chloride in the presence of pyridine or other suitable organic bases; the hydroxy-acids do not show this behaviour. Phenyl sulphite, b. p. 185°/15 mm. (in hydrogen); *o*-tolyl sulphite,  $\text{SO}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , b. p. 192° (corr.)/13 mm.; *m*-tolyl sulphite, b. p. 195—196° (corr.)/12 mm.; and *p*-tolyl sulphite, b. p. 199° (corr.)/12 mm., were obtained by the interaction of phenol or the cresol with thionyl chloride in the presence of pyridine and carbon disulphide; they are very stable towards water and aqueous alkalis, whereas some of their homologues, especially such as contain negative groups, readily undergo decomposition. The following compounds of this type were also prepared: *thymyl sulphite*,  $\text{SO}(\text{O}\cdot\text{C}_6\text{H}_3\text{Pr}^2\text{Me})_2$ ;  *$\alpha$ -naphthyl sulphite*,  $\text{SO}(\text{O}\cdot\text{C}_{10}\text{H}_7)_2$ , indistinct crystals, m. p. 92—93°;  *$\beta$ -naphthyl sulphite*, nacreous powder, sensitive to water; *p*-chlorophenyl sulphite,  $\text{SO}(\text{O}\cdot\text{C}_6\text{H}_4\text{Cl})_2$ , b. p. 213—214°/12 mm., solidifiable to a crystalline solid. D. F. T.

[*p*-Acetylaminophenyl Allyl Ether.] SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1263238).—*p*-Acetylaminophenyl allyl ether, leaflets, m. p. 94°, readily soluble in alcohol, ether, or acetone, but less readily so in hot water, acts as a narcotic, having also sedative and antineuralgic properties. T. F. B.

[Preparation of Bromodiethylacetylurethanes of *N*-Acylated *p*-Aminophenols.] FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Brit. Pat. 114680; U.S. Pat. 1256293 [SYNTHETIC PATENTS Co.]).—Compounds of the general formula



are obtained by the interaction of *N*-acyl derivatives of *p*-aminophenols and bromodiethylacetylcarbimide, or of *p*-acetylaminophenol-

urethanes and bromodiethylacetyl haloids. The bromodiethylacetylurethane of *p*-acetylaminophenol, white leaflets, m. p.  $144^{\circ}$ , is almost tasteless, and is readily soluble in alcohol or acetone, sparingly so in benzene, ether, or water. The bromodiethylacetylurethane of *p*-hydroxyphenylcarbamide melts at  $187^{\circ}$ . The compounds are of value as nervines and sedatives. A. S.

**Compounds of Bivalent Cobalt with Catechol.** R. F. WEINLAND and ANNA DÖTTINGER (*Zeitsch. anorg. Chem.*, 1918, **102**, 223—240).—Compounds have already been described in which the catechol residue ( $C_6H_4O_2$ ) is combined with ferric iron (A., 1912, i, 184, 445) or aluminium (A., 1914, i, 525) to form a complex anion. A series of similar catechol derivatives containing cobalt is now described, a number of ammonium, pyridine, and potassium salts of the complex acid having been prepared. The salts are obtained, in general, by addition of alkali or base to an aqueous solution containing catechol and a suitable cobalt salt, for example, sulphate or acetate, in the requisite proportions. The composition of the precipitated salt depends principally on the quantity of base or alkali added; one or two molecular proportions of alkali throw down the complex cobalto-acid, whilst increasing quantities transform this into a complex salt.

The following five compounds were obtained when ammonia was used as a precipitant. In the formulæ, R stands for the catechol residue ( $C_6H_4O_2$ ):

I.  $[CoR_2]H_2, 5\frac{1}{2}H_2O$ , bright red, four- or six-sided prisms, sparingly soluble in water. It is produced by the further action of ammonia on V.

II.  $[CoR_2](NH_4)_2$ , red, slender, rectangular prisms, very sparingly soluble in water. It is formed by the action of excess of ammonia on V.

III.  $3[CoR_2]H \cdot NH_4 + [CoR_2](NH_4)_2, H_2O$ , bright, red crystal aggregates, sparingly soluble in water. The salt is stable in contact with its mother liquor, but quickly decomposes after separation therefrom.

IV.  $[CoR_3](NH_4)_4, C_6H_4(OH)_2$ , pale red, thin tablets, easily soluble in water. The isolation of this and the previous compound requires special precautions, for which the original must be consulted.

V.  $Co_3R_2(OH)_2, 6H_2O$ , a pale red, sparingly soluble powder, always precipitated first when ammonia is added to a solution containing catechol and a cobalt salt.

Only a single compound was obtained when pyridine was substituted for ammonia.

VI.  $4[CoR_3]H_2, (C_5H_5N)_3, C_6H_4(OH)_2$ , a sparingly soluble, flesh-coloured, minutely crystalline precipitate.

Compounds I. and V. can both be obtained by addition of potassium hydroxide solution in limited quantity to a catechol-cobalt solution. Using increased quantities of the hydroxide, two potassium salts were obtained.

VII.  $[\text{CoR}_2]\text{KH}_2\text{H}_2\text{O}$ , red to bluish-violet, thin oblong tablets, easily soluble in water to a dirty green solution.

VIII.  $[\text{CoR}_3]\text{K}_4\text{H}_2\text{O}$ , red, slender, four-sided, rectangular prisms, very soluble in water. The salt is formed only in very strongly alkaline solutions ( $1\text{Co} : 3\text{C}_6\text{H}_4(\text{OH})_2 : 40\text{KOH}$ ).

By merely warming a solution of cobalt acetate with catechol, a red, crystalline precipitate is formed, but this has not been investigated.

All the above compounds darken quickly on exposure to air, except the pyridine salt. They are stable to alkalis, in which they dissolve with a reddish-violet colour. Ammonium sulphide decomposes them with precipitation of cobalt sulphide, and they are also decomposed on boiling with potassium cyanide, potassium cobalticyanide being formed. The complex cobalt-catechol anion is, therefore, less stable than the ferri-catechol anion, which is not decomposed by these reagents. The cobalto-salts do not show the intense colour characteristic of the ferric salts.

The constitution of the salts is discussed and co-ordination formulæ are suggested.

E. H. R.

#### Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. II. RALPH C. HUSTON

and THEODORE E. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1918, **40**, 785-793. Compare A., 1917, i, 19).—When aluminium chloride is added to a mixture of phenylmethylcarbinol and benzene at such a rate that the temperature is maintained at 25–35°, the reagents being in molecular proportions, *as*-diphenylethane is obtained in approximately 20% yield, together with ethylbenzene, diphenylmethane, and anthracene, these by-products being formed by the further action of aluminium chloride. By keeping the temperature below 10° and using only a semi-molecular proportion of aluminium chloride and a five-fold molecular proportion of benzene, the yield of diphenylethane is raised to 65%.

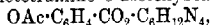
Phenylethylcarbinol, benzene, and aluminium chloride in molecular proportions at 35–40° yield 23–25% of *aa*-diphenylpropane, together with propylbenzene, diphenylmethane, and anthracene; by modifying the conditions, as in the preceding case, the yield of diphenylpropane can be raised to 40% of the theoretical.

Benzhydrol reacts with benzene (5 mols.) and aluminium chloride (1 mol.) at 35–40°, giving a yield of 40% of triphenylmethane, accompanied by diphenylmethane; with the reaction effected below 10°, the yield of triphenylmethane is 65–70%.

D. F. T.

#### Preparation of a Derivative of Hexamethylenetetramine.

LEO EGGER (D.R.-P., 303450, 1915; from *Chem. Zentr.*, 1918, i, 499).—Hexamethylenetetramine *o*-acetoxybenzoate,



m. p. 118–119°, is prepared by the gradual addition of hexamethylenetetramine (1 mol.) to a solution of *o*-acetoxybenzoic acid (1 mol.) in a restricted volume of ether.

D. F. T.

**Preparation of Tropic Acid.** CHEMISCHE WERKE GRENZACH (D.R.-P., 302737, 1917; from *Chem. Zentr.*, 1918, i, 396).—Ethyl hydroxymethylenephylacetate is reduced to ethyl tropate and hydrolysed, the resulting tropic acid being identical with the product obtained from atropine. D. F. T.

**A New Method for the Preparation of Aldehydes. I.** KARL W. ROSENMUND (*Ber.*, 1918, 51, 585—594).—The author has discovered the conditions whereby acyl chlorides can be converted into the corresponding aldehydes by means of hydrogen in the presence of a catalyst. The method gives excellent results and promises to be the best yet devised for the preparation of aldehydes.

The best conditions are far from what might have been predicted. The most suitable catalysts are palladinised barium sulphate containing about 5% of metal, and Kelber's nickel catalyst (A., 1917, ii, 215). The chloride is dissolved in three to five times its volume of dry xylene or cumene, which are usually regarded as "poisonous" to catalysts, and the solution is actually boiled in a reflux apparatus, hydrogen being bubbled through the while and the hydrogen chloride escaping. Even if the chloride contains traces of phosphoryl chloride, the reduction proceeds smoothly. The aldehyde is subsequently removed by means of sodium hydrogen sulphite or distillation, and the yields are often very high.

As examples, the following preparations are described; benzaldehyde from benzoyl chloride, yield 97%; butyraldehyde from butyryl chloride, yield 50%; stearaldehyde from stearyl chloride; *p*-methylcarbonatobenzaldehyde,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , radial aggregates of needles, m. p.  $18.5^\circ$  (*phenylhydrazone*, m. p.  $157\text{--}158^\circ$ ), from *p*-methylcarbonatobenzoyl chloride, yield 95%. J. C. W.

**A New Method for the Preparation of Aldehydes. II. Synthesis of Gallaldehyde.** KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1918, 51, 594—602).—The carbomethoxy- and acetyl derivatives of gallic acid are converted into the chlorides, these reduced to the aldehydes by the new method (preceding abstract), and then hydrolysed to gallaldehyde.

3:4:5-Trimethylcarbonatobenzaldehyde,  $\text{CHO}\cdot\text{C}_6\text{H}_2(\text{O}\cdot\text{CO}_2\text{Me})_3$ , is a resinous mass, and its *p*-nitrophenylhydrazone is also viscous. 3:4:5-Triacetoxybenzaldehyde, from triacetylgalloyl chloride (this vol., i, 173), is also resinous, but its *p*-nitrophenylhydrazone separates in lemon-yellow, cruciform groups of fan-like crystals, m. p.  $186\text{--}187^\circ$  (decomp.). These aldehydes are hydrolysed in an atmosphere of hydrogen, the former by means of 2*N*-sulphuric acid at  $0^\circ$ , the latter by boiling with alcoholic potassium acetate. Gallaldehyde (3:4:5-trihydroxybenzaldehyde) crystallises from water with  $11\text{H}_2\text{O}$ , which it slowly loses in a desiccator, becoming yellow. It has m. p.  $212^\circ$  (decomp.), does not precipitate gelatin, reduces ammoniacal silver and Fehling's solutions immediately, develops a golden-yellow colour when shaken with calcium cyanide solution, and an inky-blue with ferric chloride. The *p*-nitro-

*phenylhydrazone* forms golden-yellow, feathery needles, m. p. 234—236° (decomp.), but the aldehyde is so strongly acidic that it also yields a *p*-nitrophenylhydrazine salt of its *p*-nitrophenylhydrazone, in bundles of stout, yellowish-red needles, m. p. 202—204° (decomp.). On methylation with methyl sulphate, the aldehyde yields the known 3 : 4 : 5-trimethoxybenzaldehyde (Mauthner, A., 1908, i, 348).

Nierenstein (A., 1909, i, 402) believed he had isolated gall-aldehyde by the hydrolysis of acetylleucotannin, but according to his account it separated spontaneously from a solution containing not more than 1% of the aldehyde in alkali carbonate. As the aldehyde is more acidic than acetic acid, and freely soluble in water and alkali carbonates, it is improbable that Nierenstein encountered the compound.

J. C. W.

#### Preparation of Salts of Anthraquinonesulphonic Acids.

THE BARRETT CO. (U.S. Pat. 1260535).—Anthraquinonemonosulphonic acid may be separated from the disulphonic acids by treating a solution of the acids with sodium sulphate, whereon the monosulphonic acid is precipitated as its sparingly soluble sodium salt.

A. S.

#### Constituents of Essential Oils. Betulol. F. W. SEMMLER,

K. G. JONAS, and W. RICHTER (*Ber.*, 1918, 51, 417—424).—From an examination of betulol, an ingredient of birch bud oil (compare von Soden and Elze, A., 1905, i, 451), the conclusion is drawn that the compound is a bicyclic sesquiterpene alcohol of the terpene type.

Betulol,  $C_{15}H_{24}O$ , has b. p. 157—158°/13 mm.,  $D^{16}_D$  0.9777,  $n^{20}_D$  1.5150,  $\alpha^{20}_D$  -26.5°, and betulyl acetate (*ibid.*) has b. p. 158—165°/10 mm.,  $D^{20}_D$  0.9854,  $n^{20}_D$  1.4962,  $[\alpha]^{20}_D$  -12°. Betulol slowly absorbs hydrogen in the presence of platinum, yielding *tetrahydrobetulol*, b. p. 153—158°/14 mm.,  $D^{18}_D$  0.9415,  $n^{18}_D$  1.4908,  $\alpha^{18}_D$  -6.8°, and a small quantity of bicyclic *tetrahydrobetulene*,  $C_{15}H_{22}$ , b. p. 118—120°/11 mm.,  $D^{18}_D$  0.8737,  $n^{18}_D$  1.4744,  $\alpha^{18}_D$  -3°, this being derived from the product of the elimination of water from betulol. *Betulyl chloride*, obtained by means of phosphorus pentachloride, has b. p. 160—170°/11 mm.,  $D^{21}_D$  1.0145,  $n^{21}_D$  1.5208,  $\alpha^{21}_D$  +9.4°, but this is obviously a mixture, for it yields an inseparable mixture of bi- and tri-cyclic *betulenes*,  $C_{15}H_{24}$ , on pouring its alcoholic solution on hot sodium. The molecular refraction of the latter mixture affords the clue to this, and it is explained by the fact that hydrogen chloride, generated during the action of the phosphorus pentachloride, effects ring closure to a certain extent. Treatment of the chloride with calcium oxide at 95° also indicates the presence of a mixture, for the products are bicyclic *dehydrobetulene*,  $C_{15}H_{22}$ , b. p. 112—114°/9 mm.,  $D^{23}_D$  0.9186,  $n^{23}_D$  1.5052,  $\alpha^{23}_D$  -68°, and tricyclic *betulol*,  $C_{15}H_{24}O$ , which crystallises in silky needles, m. p. 147—148°, b. p. 160—166°/13 mm., and forms an *acetate*, b. p. 170—176°/13 mm.,  $D^{22}_D$  1.0290,  $n^{22}_D$  1.5046,  $\alpha^{22}_D$  +10°.

J. C. W.

**Japanese Oil of Peppermint.** HEINRICH WALBAUM (*J. pr. Chem.*, 1917, [ii], **96**, 245—250).—By the hydrolysis of the fraction of Japanese peppermint oil, b. p. 250—310°,  $D_{20}^{25}$  0.9490, there is obtainable  $\Delta^1$ -hexen- $\alpha$ -ol,  $\text{CHET:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 55—56°/9 mm., 156—157°/atmos. press.,  $D_{20}^{25}$  0.8508,  $n_D^{20}$  1.48030, the constitution of which is proved by its oxidation with potassium permanganate to propionic acid;  $\Delta^2$ -hexenaldehyde, b. p. 140—155° (semicarbazone, m. p. 163°), and the oily  $\Delta^2$ -hexenoic acid, b. p. 215—218° (Fittig and Baker, A., 1895, i, 206, give b. p. 216—217°), are also obtained, together with the hexenyl hexenoate, on oxidation of the alcohol with chromic acid. The hexenyl alcohol is present in the peppermint oil in the form of  $\Delta^2$ -hexenyl phenylacetate,  $\text{C}_{14}\text{H}_{18}\text{O}_2$ ; the pure, synthetically prepared ester is a liquid of clinging, onion-like odour, b. p. 135—136°/4 mm., 299°/760 mm.,  $D_{20}^{25}$  1.000,  $n_D^{20}$  1.49810; the benzoate, b. p. 134—135°/6 mm.,  $D_{20}^{25}$  1.0083,  $n_D^{20}$  1.50560, possesses a fainter odour than the phenylacetate; the acetate, b. p. 75—76°/23 mm.,  $D_{20}^{25}$  0.9077,  $n_D^{20}$  1.42355, has a pleasant odour recalling radishes, whilst the formate, b. p. 66°/35 mm.,  $D_{20}^{25}$  0.9149,  $n_D^{20}$  1.42685, has a similar but rather more pungent odour; the hydrogen phthalate,  $\text{C}_{14}\text{H}_{16}\text{O}_4$ , is an oil, the silver salt of which crystallises in prisms. With phenylcarbimide, the hexenyl alcohol yields no solid product, but when treated with naphthylcarbimide, a crystalline naphthylurethane,  $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$ , m. p. 70—71°, is obtained. D. F. T.

**Saponins.** L. SPIEGEL and ARTHUR MEYER (*Ber. Deut. pharm. Ges.*, 1918, **28**, 100—126).—An examination of the saponin mowrin, obtainable from the seeds of *Bassia longifolia* (Mowrah seeds), the results of which diverge considerably from those of Moore, Sowton, Baker-Young, and Webster (A., 1910, ii, 228).

Crude mowrin consists mainly of a substance approximating to the composition  $\text{C}_{42}\text{H}_{88}\text{O}_{25}$ , easily soluble in alcohol, together with a sparingly soluble substance approximating to  $\text{C}_{42}\text{H}_{88}\text{O}_{27}$ . On hydrolysis with aqueous mineral acid, the main constituent gives rise to levulose, arabinose, and mowric acid, the latter comprising a crystalline mowragenic acid,  $\text{C}_{19}\text{H}_{28}\text{O}_5$  (sodium salt sparingly soluble), and an amorphous, mowragenic acid,  $\text{C}_{19}\text{H}_{26}\text{O}_6$ . By effecting the hydrolysis of mowrin with dilute acetic acid, it is possible to detect an intermediate product, namely, a pentoside, probably of the composition  $\text{C}_{29}\text{H}_{50}\text{O}_{16}$ . The ease with which mowrin undergoes hydrolysis is shown by the fact that on benzoylation it and mowric acid yield the same benzoyl derivative, whilst the product obtained on acetylating mowrin with sodium acetate and acetic acid appears to be derived from the above intermediate pentoside compound.

On treatment with manganese dioxide and sulphuric acid, mowric acid undergoes oxidation and polymerisation with formation of *didehydromowric acid*,  $\text{C}_{38}\text{H}_{46}\text{O}_9$ , m. p. 163°, whereas hot 35% nitric acid produces *nitrodehydromowric acid*,  $\text{C}_{19}\text{H}_{23}\text{O}_5\cdot\text{NO}_2$ , m. p. 207°, the reduction of which with stannous chloride gives a *hydroxydehydromowric acid*,  $\text{C}_{19}\text{H}_{23}\text{O}_5\cdot\text{OH}$ , m. p. 200° (*trimethyl deriv-*

ative, m. p. 183°; *diethyl* derivative, m. p. 136°). More energetic nitration of mowric acid gives rise to a nitro-compound,

$\text{C}_{17}\text{H}_{21}\text{O}_5\cdot\text{NO}_2$   
or  $\text{C}_{17}\text{H}_{19}\text{O}_5\cdot\text{NO}_2$ , m. p. 210°, which is reducible to a hydroxy-compound,  $\text{C}_{17}\text{H}_{19}\text{O}_5\cdot\text{OH}$ , m. p. 170° (*trimethyl* derivative, m. p. 142°; *diethyl* derivative, m. p. 150°). This nitro-compound is oxidisable by hydrogen peroxide and by potassium permanganate with sulphuric acid, giving substances  $\text{C}_{17}\text{H}_{18}\text{O}_5(\text{OH})_2$ , m. p. 125°, and  $(\text{C}_{17}\text{H}_{10}\text{O}_6)_2\text{O}$ , m. p. 164°, respectively, whilst hydriodic acid converts its reduction product into a substance  $\text{C}_{17}\text{H}_{21}\text{O}_5\text{I}$  or  $\text{C}_{17}\text{H}_{23}\text{O}_5\text{I}$ , m. p. 174°. Fusion with potassium hydroxide converts mowric acid into a substance  $\text{C}_{14}\text{H}_{15}\text{O}_3$ , m. p. 181° (*methyl* derivative, m. p. 160–175°).  
D. F. T.

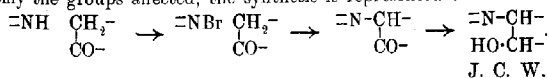
**The Action of Sunlight on Coumarin.** A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 875–876. Compare Ciamician and Silber, A., 1914, ii, 234).—A preliminary account of experiments which indicates that the product of sunlight on coumarin is not the hydrodicoumarin which was obtained synthetically by Fittig and Dyson in 1889 (compare Dyson, T., 1887, **51**, 66).  
S. B. S.

**Synthesis of Pyranol Derivatives.** SARAT CHANDRA CHATTERJI and BROJENDRA NATH GHOSH (T., 1918, **113**, 444–449).—Diketohydrindene condenses with *o*-hydroxyaldehydes, giving ketoinopyranol derivatives (compare T., 1915, **107**, 1442), this reaction being due, apparently, to the presence of the group  $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$  in the diketohydrindene. In order to show that the reaction is a general one, two other ketones, benzoylacetone and acetylacetone, containing this group have been condensed with salicylaldehyde.

Benzoylacetone, when condensed with salicylaldehyde in methyl alcohol solution in the presence of hydrogen chloride, gave 3-*acetyl*-2-*phenyl*-1:4-benzopyranol anhydrohydrochloride and 3-benzoyl-2-methyl-1:4-benzopyranol anhydrohydrochloride, together with a third compound,  $\text{C}_{27}\text{H}_{20}\text{O}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ , m. p. 120°.

With acetylacetone, salicylaldehyde gave a compound,  $\text{C}_{17}\text{H}_{16}\text{O}_3$ , violet prisms soluble in acetic acid, giving a hydrochloride, a phenylhydrazone, m. p. above 300°, and an insoluble compound,  $\text{C}_{23}\text{H}_{22}\text{O}_3$ . [For experimental details, see the original.] W. G.

**The Cinchona Alkaloids. XIX. Partial Synthesis of Quinine.** PAUL RABE and KARL KINDLER (*Ber.*, 1918, **51**, 466–467. Compare A., 1911, i, 742).—Quinine (quinotoxine) reacts with sodium hypobromite to form *N*-bromoquinicine, m. p. 123°. This is converted into quinone by treatment with alkali hydroxide, and the ketone is reduced to quinine by means of aluminium powder and sodium ethoxide solution. Considering only the groups affected, the synthesis is represented thus:





**$\alpha$ -Hydroxycinchonine.** E. LÉGER (*Compt. rend.*, 1918, 166, 903—906).—As a result of a study of the behaviour of  $\alpha$ -hydroxycinchonine (compare Jungfleisch and Léger, A., 1888, 380, 508; 1889, 906), the author considers that the hydroxyl group is in the side chain, the double linking in the vinyl group being satisfied during the process of hydration.  $\alpha$ -Hydroxycinchonine thus has the constitution  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot[\text{C}_{16}\text{H}_{17}(\text{CH}\cdot\text{OH})\text{N}_2]$ . The grouping  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot$  is preferred to  $\text{CH}_3(\text{OH})\cdot\text{CH}_2\cdot$ , since the compound yields (1) iodoform by the action of sodium hydroxide and iodine, and (2) carbon tetrabromide by the action of hypobromous acid.

W. G.

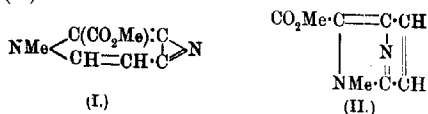
**Cevadine [Veratrine]. III.** MARTIN FREUND and ADOLF SCHWARZ (*J. pr. Chem.*, 1917, [ii], 96, 236—244. Compare A., 1904, i, 613).—As the author has been unable to confirm the results described earlier (*Zeitsch. Ver. deutsch. Chem.*, 1909, 22, 2472) on the degradation of cevine, these are withdrawn. When cevine methiodide,  $\text{C}_{27}\text{H}_{45}\text{O}_8\text{N}\cdot\text{MeI}\cdot 2\text{H}_2\text{O}$ , decomp.  $257^\circ$  (Freund and Schwarz, A., 1899, i, 465), is treated with silver oxide and water, it undergoes conversion into des-*N*-methylcevine,  $\text{C}_{28}\text{H}_{45}\text{O}_8\text{N}\cdot\text{H}_2\text{O}$ , crystalline scales, decomp. at  $277^\circ$  (accompanied by an uncrystallisable yellow oil), which absorbs atmospheric carbon dioxide, with formation of a hydrogen carbonate, and yields crystalline salts resistant to aqueous ammonia or sodium carbonate; the *hydriodide* ( $1\text{H}_2\text{O}$ ), decomp. at  $256^\circ$ , *hydrobromide*, with  $1\text{H}_2\text{O}$ , decomp. at  $271$ — $273^\circ$ , *hydrochloride*, decomp. at  $258$ — $261^\circ$ , and *picrate*, with  $3\text{H}_2\text{O}$ , were prepared. Methyl iodide at  $60$ — $70^\circ$ , cyanogen bromide, phenylhydrazine, hydroxylamine, semicarbazide, thiosemicarbazide, and aqueous hydrogen peroxide left the cevine molecule intact. Treatment of a methyl-alcoholic solution of de-*N*-methylcevine hydrochloride with silver oxide yields an alkaline solution, which, on evaporation, leaves an oily residue; this, on the addition of alkali and warming, changes into the crystalline solid base, the behaviour being suggestive of a tautomeric change from a true ammonium base to a pseudo-base.

Examination of cevadine, cevine, and dibenzoylcevine by Zerewitinoff's method with a solution of methyl magnesium iodide in *iso*amyl ether indicates the presence of four, six, and six hydroxyl groups respectively, the unexpected value for the last figure being at present without explanation.

D. F. T.

**Ricinine.** BRUNO BÖTTCHER (*Ber.*, 1918, 51, 673—687).—The most important study of ricinine, the alkaloid of castor-oil seeds, which has appeared so far is that by Maquenne and Philippe, who went so far as to assign the formula (I) to the compound (A., 1905, i, 80). In view of the very unusual three-membered nitrogen-carbon ring in this formula, the author has

made a fuller examination of ricinine, and proposes the formula (II):



This accords with the behaviour of ricinine at one and the same time as the ester of a pyridinecarboxylic acid and as a glyoxaline.

The alkaloid is obtained by extracting the residue of the seeds with boiling water, after removing the oil, evaporating the extract to dryness under reduced pressure, and exhausting the powder with alcohol. From 300 kilos. of seed, about 450 grams of crude alkaloid may be obtained. The pure compound has m. p. 200–201°, reduces permanganate at once, is not affected by nitric acid, and, like histidine, gives Weidel's reaction. On hydrolysis with dilute potassium carbonate, it yields ricininic acid, m. p. 296–298° (decomp.), which forms a *silver* salt, from which ricinine may be recovered by means of methyl iodide. The acid may be reduced by means of 5% sodium amalgam to *dihydroricininic acid*, which crystallises from water in white needles, m. p. 245° (if quickly heated), 255° (if slowly heated), which give an intense violet coloration with ferric chloride, characteristic of glyoxaline-carboxylic acids. The *methyl ester* (*dihydroricinine*), prepared from the *silver* salt, but not by reducing ricinine itself, crystallises in glistening needles or plates, m. p. 160°, and is much more easily hydrolysed than ricinine. The failure to obtain a tetrahydro-derivative is an argument in favour of formula (II) as against (I); the ethylene linking in the glyoxaline ring is, as usual, unaffected by sodium amalgam.

Ricininic acid is oxidised by chromic acid and dilute sulphuric acid to methylamine, oxalic acid, and hydrogen cyanide, the evolution of this being quantitative, one molecule per molecule of acid, and characteristic also of histidine. Hypobromite solutions apparently cause saturation of the ethylene linking, a *compound*, m. p. 256–257° (decomp.), represented by the formula  $\text{HBrO}\cdot\text{C}_7\text{H}_6\text{O}_2\text{N}_2$  (ricininic acid), crystallising on acidifying. Distillation with zinc dust furnishes a dipyril (*aurichloride*,  $\text{C}_{10}\text{H}_8\text{N}_2\cdot\text{H}\cdot\text{AuCl}_4$ , decomp. 250°) and a pyrrole derivative. Distillation with lime also gives a pyrrole compound, which is another established reaction of histidine.

Ricininic acid is degraded to 3-hydroxy-1-methyl-1:4-dihydro-pyrid-4-one,  $\text{NMe} < \begin{array}{c} \text{CH}=\text{CH} \\ \text{CH}\text{:C}(\text{OH}) \end{array} > \text{CO}$ , by means of fuming hydrochloric acid at 150° (the best method; see Maquenne and Philippe, A., 1904, i, 339), or by hydrolysis with alkali hydroxides. If heated with 50% sulphuric acid, an *acid* is produced, m. p. 216° (decomp.), which contains one NMe group, gives the reddish-brown colour with ferric chloride characteristic of pyridine-carboxylic

acids, yields a pyrrole on distillation with lime, and forms the above pyridone on heating with hydrochloric acid at 150°. The pyridone does not give the pyrrole reaction on distillation with lime.

J. C. W.

**Synthesis of  $\alpha$ -Piperidylethylalkine (2- $\alpha$ -Hydroxypropyl-piperidine).** LUDWIG LAUTENSCHLÄGER and ARVID G. T. ÖNSÄGER (*Ber.*, 1918, **51**, 602—605).—Pyridine-2-aldehyde (Harries and Lénárt, A., 1915, i, 970) is converted into 2- $\alpha$ -hydroxypropylpyridine, b. p. 214—216° (Engler and Bauer, A., 1891, 1505) by means of magnesium ethyl bromide, and this is reduced by sodium and alcohol to 2- $\alpha$ -hydroxypropylpiperidine, which crystallises from light petroleum in leaflets, m. p. 99—100°, and needles, m. p. 69—70° (*ibid.*, 1894, i, 471). A small quantity of *r*-coniine is formed as well.

J. C. W.

**Transformation of Unimolecular *N*-Alkyldihydroquin-aldine Picrates.** GUSTAV HELLER (*Ber.*, 1918, **51**, 437—439).—The picrates of 1:2-dimethyl- and 2-methyl-1-ethyl-1:2-dihydroquinoline (A., 1915, i, 300; and Freund, A., 1905, i, 151; 1909, i, 417) suffer rearrangement on crystallisation from acetone and light petroleum into bright red *isomerides* (1-methyl-, m. p. 148°; 1-ethyl-, m. p. 128°). These do not yield the parent bases on treatment with sodium hydroxide, but change into the *sodium* salts of third, acidic *isomerides* (1-methyl-, m. p. 129—131°; 1-ethyl-, m. p. 136°; both pale brown granules).

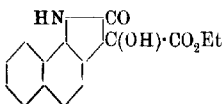
J. C. W.

**Synthesis in the  $\alpha$ -Naphthindole Series.** J. MARTINET (*Compt. rend.*, 1918, **166**, 851—853. Compare A., 1913, i, 756).— $\alpha$ -Naphthylamine condenses with ethyl mesoxalate in boiling acetic acid solution to give *ethyl 3-hydroxy-2-oxynaphthindole-3-carboxylate* (annexed formula), m. p. 201°.

The corresponding *methyl* ester has m. p. 268°. Either of these esters, when heated in a water-bath with aqueous potassium hydroxide in a current of hydrogen, and the liquid then acidified, yields  $\alpha$ -naphthorindole, m. p. 247°. These esters, when treated with aqueous potassium hydroxide in contact with air, yield potassium  $\alpha$ -naphthisatate, from which, when the solution is acidified,  $\alpha$ -naphthisatic acid is precipitated, which is rapidly converted into  $\alpha$ -naphthisatin, red needles, m. p. 225° (compare Hinsberg, A., 1888, 373). Contrary to the statement of Hinsberg (*loc. cit.*), this isatin gives the indophenine reaction, and its phenylhydrazone has m. p. 286°, and not 270°, as stated (*loc. cit.*).

W. G.

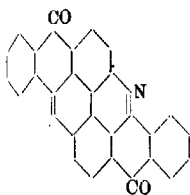
**Preparation of Mercury Compounds of the Acridine Series.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1259517).—The mercury compounds obtained by treating acridine dyes, alkylated at the acridine nitrogen atom, with a soluble mercury salt in the presence of a solvent, are yellowish-brown powders,



giving yellowish-green solutions in water, yellowish-green fluorescence in dilute solution in alcohol, ethyl acetate, glacial acetic acid, and acetone, and an intense green fluorescence in concentrated sulphuric acid. Even in very dilute solutions they check the growth of bacteria. The mercury compound of the product obtained by heating 3:6-diamino-2:7-dimethylacridine with methyl chloride under pressure, is specially claimed.

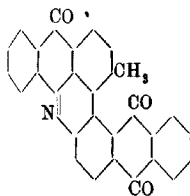
A. S.

**Pyranthridone.** ROLAND SCHOLL and OTTO DISCHENDORFER (*Ber.*, 1918, 51, 441—452).—Pyranthridone (annexed formula) may be

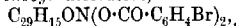


regarded as a compound intermediate between pyranthrone,  $C_{30}H_{14}O_2$ , and flavanthrene,  $C_{26}H_{12}O_2N_2$ . Its synthesis is now described. 1-Chloro-2-aminoanthraquinone (A., 1913, i, 1070) is boiled with benzaldehyde, the water produced being allowed to escape, when 1-chloro-2-benzylideneaminoanthraquinone is formed, in pale yellow leaflets, m. p.  $184^\circ$ . This is boiled with 1-chloro-2-methylanthraquinone in naphthalene solution, with a little

copper powder, when a mixture of dianthraquinonyls is obtained, consisting of condensation products of each of the reacting compounds separately and the desired unsymmetrical 2-benzylidene-amino-2'-methyl-1:1'-dianthraquinonyl. After removing the solvent naphthalene by steam, the residue is dissolved in concentrated sulphuric acid, whereby the 2:2'-dimethyl-1:1'-dianthraquinonyl is unchanged, but the benzylidene residues from the other products are eliminated as benzaldehyde. The 2:2'-diamino-1:1'-dianthraquinonyl so formed immediately condenses to flavanthrene and the 2-amino-2'-methyl-1:1'-dianthraquinonyl to 3:4-phthalyl-8:9-o-benzoylene-5-methylphenanthridine (annexed



formula). The latter is moderately soluble in hot nitrobenzene, whereas flavanthrene is almost insoluble, and the other products are freely soluble. It crystallises in golden, rhombic leaflets, which do not melt below  $450^\circ$ . Reduction with hyposulphite at  $30-40^\circ$  gives a red vat, from which a di-p-bromobenzoyl derivative,



small, yellow needles, m. p.  $318^\circ$ , may be prepared, whilst reduction with strongly alkaline solutions of hyposulphite at higher temperatures yields a blue vat, from which a di-p-bromobenzoyl-derivative,  $C_{29}H_{17}ON(O-CO-C_6H_4Br)_2$ , m. p.  $210^\circ$ , may be obtained.

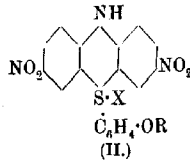
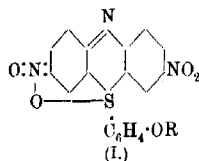
The phenanthridine derivative may be condensed to pyranthridone by heating alone at  $360-380^\circ$ , or with sulphuric acid at  $160-170^\circ$ , or with alcoholic potassium hydroxide. The dye crystallises from quinoline in brownish-yellow needles, which sublime on heating, but are not molten at  $500^\circ$ . It yields a violet-blue

vat, from which cotton is dyed orange-red after hanging in the air. A *di-p-bromobenzoyl* derivative, felted, orange-yellow needles, decomp.  $350^{\circ}$ , may also be obtained from the tetrahydro-compound in the vat. When heated with hydriodic acid and phosphorus, pyranthridone yields *dihydropyranthridine*,  $C_{20}H_{19}N$ , in pale yellow, rhombic leaflets, m. p.  $302^{\circ}$ , which is converted into the parent base, *pyranthridine*,  $C_{20}H_{17}N$ , reddish-brown leaflets, m. p.  $370^{\circ}$ , by passing its vapour over red-hot copper. J. C. W.

**Synthesis of Flavanthrene.** R. SCHOLL and O. DISCHENDORFER (*Ber.*, 1918, **51**, 452—453).—The immediate precursor of flavanthrene in the various syntheses which have been achieved is 2:2'-diamino-1:1'-dianthraquinonyl, but this has not hitherto been isolated. It may be prepared by boiling 1-chloro-2-benzylidenaminoanthraquinone with copper powder and naphthalene (compare preceding abstract), extracting the 2:2'-dibenzylidenamino-1:1'-dianthraquinonyl so formed with cold alcohol, and leaving the solution for some time, when the benzylidene residues are spontaneously eliminated and the desired compound crystallises. It forms microscopic, red needles, and changes into flavanthrene at  $250^{\circ}$ . J. C. W.

**The Properties of the Sulphonium Compounds obtained by S. Smiles by the Condensation of Dinitrophenythiazine-sulphoxide with Aromatic Amines, Phenols, and Phenol-ethers.** F. KEHRMANN, S. LIEVERMANN, and P. FRUMKINE (*Ber.*, 1918, **51**, 474—480).—A revision and criticism of the work of Smiles and Hilditch (*T.*, 1908, **93**, 145). It appears that the products obtained by these workers were abnormally coloured by impurities, although their constitution was rightly interpreted.

It is essential to use pure 3:9-dinitrophenythiazine-sulphoxide, prepared as in A., 1913, i, 1231, for the condensations, and the reaction with anisole or phenetole is best brought about by shaking a mixture of the compounds with concentrated sulphuric and acetic acids (1:1). The phenazothionium salts so produced are converted into the free bases by precipitation with ammonia. 3:9-Dinitro-1-anisylphenythiazine, m. p.  $248^{\circ}$ , forms carmine-red flocks, which change in contact with the mother liquor into a green, crystalline powder with metallic lustre, and the 1-phenetyl compound, m. p.  $230^{\circ}$ , crystallises in groups of fiery-red prisms or dark red granules with green lustre. The free bases resemble rosindone, and their solutions exhibit a brilliant orange-yellow fluorescence, whilst solutions of their salts are pale in colour and not fluorescent. The

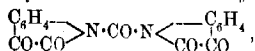


free "bases" are therefore para-quinonoid, internal phenazothionium salts of nitronic acid (I), whilst the salts of mineral acids (II) contain nitro-groups as the sole chromophores.

The *chloride* of the anisyl derivative forms straw-yellow granules, the *platinichloride* is pale yellow, and the *dichromate* is egg-yellow.

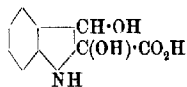
The anisyl compound has also been reduced by means of stannous chloride, the stannichloride so formed acetylated, and the new canary-yellow base, 3:9-diacetyl-amino-1-anisylphenazothionium, isolated as the *hydrogen carbonate*, which forms satiny scales, the *platinichloride* being very pale yellow. J. C. W.

**Syntheses in the Isatin Series.** "Definitive Enzymic Synthesis." GUSTAV HELLER (*Ber.*, 1918, 51, 424—437).—*N*-Sodioisatin reacts readily with organic chlorides at moderate temperatures in the presence of benzene. Thus, acetyl chloride yields *N*-acetylisatin, m. p. 141°; benzenesulphonyl chloride gives *N*-benzenesulphonylisatin, in pale yellow, slanting prisms, m. p. 186.5—187°; carbonyl chloride forms *carbonyldi-isatin*,



in long, yellow needles, m. p. 218° (decomp.); ethyl chloroformate yields *ethyl isatin-1-carboxylate*, in yellow prisms, m. p. 117°, which forms a *dioxime*, needles, m. p. 145°, and the corresponding *methyl ester* crystallises in golden-yellow leaflets, m. p. 170°.

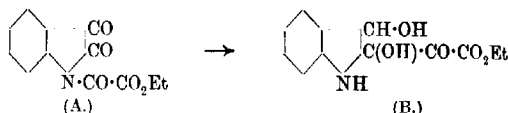
The latter esters undergo a remarkable change when boiled with water, left with 50% sulphuric acid or concentrated hydrochloric acid, or treated with zinc dust and acetic acid. The product is an acid with four atoms of hydrogen more than the parent 1-carboxylic compound; it does not give the indophenine reaction, but it very readily yields isatinic acid when exposed in alkaline solutions to the air. Acetaldehyde is also produced if the ethyl ester is used, and formaldehyde from the methyl ester. The acid is therefore 2:3-dihydroxy-2:3-dihydroindole-2-carboxylic acid



(annexed formula); it forms colourless crystals, m. p. 144°, and yields a *phenyl-hydrazide*, pale yellow, narrow prisms, m. p. 152° (decomp.), and a *lactone*, long, yellow needles, m. p. 108°. The corresponding esters, *ethyl*, m. p. 67°, and *methyl*, m. p. 85°, are produced when the original esters are boiled with the alcohols. Acetaldehyde and formaldehyde are also produced, but the origin of the four hydrogen atoms is obscure. As a rule, it is by no means easy to convert an indole derivative into a dihydroindole compound, but the above reaction indicates that when the carbalkyloxy-group is introduced into isatin, the subsequent fixation of as many as four atoms of hydrogen, and a thorough internal rearrangement in the molecule, become very easy. The change resembles the far-reaching effects so often produced by enzymes, and the fact that acids stimulate the change only strengthens the analogy.

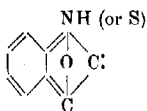
The acid undergoes another remarkable change on oxidation with potassium dichromate and dilute sulphuric acid. The product is an acid which contains an extra methylene group and yields quinaldic acid on reduction with hydriodic acid and phosphorus. It is therefore 2:4-dihydroxy-1:2:3:4-tetrahydro-quinoline-2-carboxylic acid,  $C_6H_4 \begin{smallmatrix} CH(OH) \cdot CH_2 \\ \diagup \quad \diagdown \\ NH \quad C(OH) \cdot CO_2H \end{smallmatrix}$ ; it forms long needles, m. p. 127°, yields a methyl ester, m. p. 62°, and gives a hydroxydihydroquinoline-2-carboxylic acid, m. p. 184°, on heating with acetic anhydride and sodium acetate. This obscure case of the extension of the ring from five members to six also recalls enzyme activities.

*N*-Sodioisatin also reacts with ethyl oxalyl chloride, forming *N*-ethyloxalato-isatin [*ethyl isatin-1-glyoxylate*] (A), in pale yellow needles, m. p. 180—182°, which changes into 2:3-dihydroxy-2-ethyl-oxalatodihydroindole [*ethyl 2:3-dihydroxy-2:3-dihydroindole-2-glyoxylate*] (B), m. p. 81°, when boiled with alcohol. J. C. W.



oxalatodihydroindole [*ethyl 2:3-dihydroxy-2:3-dihydroindole-2-glyoxylate*] (B), m. p. 81°, when boiled with alcohol. J. C. W.

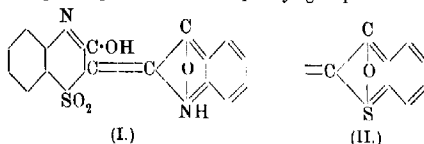
**Dyes Derived from Sulphazone. A Contribution to Claasz's New Theory of the Indigo Chromophore.** W. HERZOG (*Ber.*, 1918, 51, 516—521).—Sulphazone, which does not form an oxime or hydrazone, thus agreeing with the suggestion that it should be regarded as 3-hydroxybenzsulphonazine (A., 1916, i, 424), has often been used as a component in azo-dyes (A., 1912, i, 390). It has also been converted into benzsulphonazoline by the action of ammonia under pressure (Claasz, A., 1916, i, 425), and this has been used to prepare dyes which closely resemble indigotin without containing the usually accepted indigo chromophore,  $-\text{CO} \cdot \text{C} \cdot \text{C} \cdot \text{CO}-$ . The discovery of these dyes has led Claasz to suggest that the indigo chromophore is a quinonoid, inner-salt structure of the annexed type (A., 1916, i, 840).



It is now shown that sulphazone itself, because of its reactive methylene group, can also form vat-dyes of the indigoid type, the tinctorial properties of which can only be ascribed to the presence of the above chromophore.

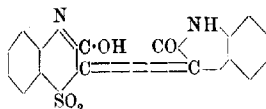
Sulphazone condenses with  $\alpha$ -isatinanilide in boiling acetic anhydride to form the compound (I). This separates in deep bluish-red crystals, which sublime at above 300°, and dissolve in concentrated sulphuric acid with violet colour and in fuming acid (20%  $\text{SO}_3$ ) with carmine colour. It is decomposed by alkalis after a time, but a fresh, yellowish-green solution in sodium hydroxide yields a red and finally yellow hyposulphite vat. The affinity for fibres is very small, however, and the colour on

filter paper changes from strawberry-red to dark green, probably owing to the participation of the sulphonyl group in the reduction.



The compound (II) is obtained by condensing sulphazone with thionaphthenequinone-anilide (A., 1908, i, 200). It forms yellowish-red needles which melt and sublime at above 300°, and although it is unstable towards alkali hydroxides, it is possible to prepare a yellow hyposulphite vat.

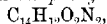
When sulphazone is condensed with  $\beta$ -isatinanilide (isatin-2-anil),



a compound is produced which is related to the above dye (I) as indirubin is to indigotin. The lack of tinctorial properties is ascribed to the absence of the above chromophore. The compound (annexed formula) forms

bluish-red crystals which decompose at about 300°, and dissolve in sulphuric acid with yellowish- to reddish-brown colour. J. C. W.

**Hydantoin Derivatives.** CLARENCE J. WEST (*J. Biol. Chem.*, 1918, **34**, 187—194).—The following hydantoin derivatives have been prepared by the method described by Dakin (A., 1910, i, 590). In view of Dakin's theory regarding the structure of allantoin (T., 1915, **107**, 434), it was thought that the active *dl*-hydantoin might be found to differ in physical properties from the inactivated forms. Such differences have not been observed. *d*- $\alpha$ -Phenylcarbamidopropionic acid,  $C_{10}H_{13}O_3N_2$ , crystallises in needles, m. p. 175° (decomp.),  $[\alpha]_D^{20} + 7.78^\circ$  in acetone; *d*- $\alpha$ -phenylmethylhydantoin,  $C_{10}H_{10}O_2N_2$ , m. p. 178°,  $[\alpha]_D^{20} + 2.24^\circ$  in *N*/2-sodium hydroxide and  $-10.04^\circ$  in acetone; *dl*- $\alpha$ -naphthylmethylhydantoin,



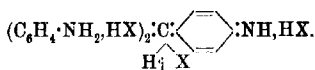
m. p. 179—180°; *d*- $\alpha$ -naphthylcarbamidopropionic acid,  $C_{14}H_{14}O_3N_2$ , needles, m. p. 198—200° (decomp.),  $[\alpha]_D^{20} + 3.80^\circ$  in *N*/2-sodium hydroxide; *d*- $\alpha$ -naphthylmethylhydantoin,  $C_{14}H_{13}O_2N_2$ , m. p. 166°,  $[\alpha]_D^{20} - 17.85^\circ$  in acetone;  $\alpha$ -carbamidobutyric acid,  $C_5H_9O_3N_2$ , m. p. 184°. The melting points of the following compounds have been determined, and found to differ from those hitherto recorded: hydantoic acid, 179—180°; *dl*-methylhydantoin, 155—156°; *dl*- $\alpha$ -phenylcarbamidopropionic acid, 174°; *dl*- $\alpha$ -phenylmethylhydantoin, 178°;  $\alpha$ -carbamido- $\alpha$ -methylpropionic acid, 184°; *dl*-hydantoin-acetic acid, 228—229°, and *dl*-hydantoinpropionic acid, 179—180°.

H. W. B.

**Constitution and Colour. VI. Triphenylmethane Dyes.** F. KEHRMANN (*Ber.*, 1918, **51**, 468—474).—The constitution of

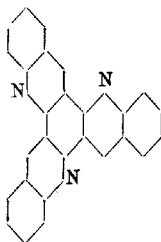


the various salts of triphenylmethane bases is discussed. Most of the facts are already known, but the theories developed are based also on the results of spectrographic observations which will be published later. The novel feature is the suggestion that the central carbon atom participates in the formation of the highest type of salts, namely, those which only exist in strongly acid solutions. The extra equivalent of acid is attached by residual or main affinities to this atom. For example, the yellow solution of triphenylmethyl chloride in a solution of hydrogen chloride in acetic acid is supposed to contain the salt,  $\text{H} \begin{array}{c} \diagup \\ \text{Cl} \end{array} \text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{H} \begin{array}{c} \diagdown \\ \text{Cl} \end{array}$  and the golden-yellow, tetra-acid salts of magenta are written

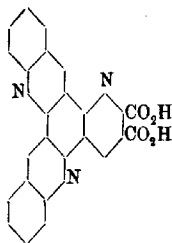


J. C. W.

**Oxidative Degradation of Phloroquinyl. I. Pyrquinacridine and its Carboxylic Acids.** L. T. BRATZ and ST. VON NIEMENTOWSKI (*Ber.*, 1918, 51, 366—376).—Phloroquinyl (I) (*A.*, 1906, i, 210) is a remarkably stable substance which can only be oxidised at all readily by means of sodium dichromate in solution in moderately concentrated nitric acid. The product of this reaction is a yellow, crystalline acid, *pyrquinacridinedicarboxylic acid* (II). It is a very sparingly soluble acid, m. p. 375°, which

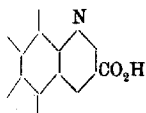


(I.)



(II.)

crystallises from much acetone in almost colourless needles with  $10\text{Me}_2$ , and from boiling glacial acetic acid in very slender needles with  $1\text{AcOH}$ , or golden-yellow prisms with  $2\text{AcOH}$ . It dissolves readily in dilute alkali hydroxides or carbonates, ammonia, or boiling sodium acetate solution, the salts being precipitated on adding an excess of the alkaline agent; the *potassium* and *silver* salts are mentioned. Heated with acetic anhydride, the acid changes into its *anhydride*, which crystallises in silky needles, m. p. 374°, whilst treatment with 20% hydrochloric acid at 180—190° results in the formation of *pyrquinacridinecarboxylic*



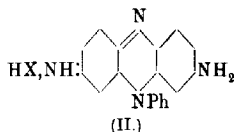
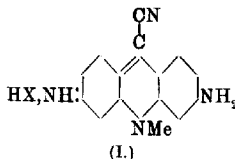
*acid* (annexed scheme). This is even less soluble than the dicarboxylic acid, but crystallises from nitrobenzene in very slender, curved needles, m. p. 380—382°. The *anilide*,  $C_{30}H_{18}ON_4$ , is obtained by cautiously heating the dicarboxylic acid with aniline, in yellow needles, m. p. 338°.

The parent substance, *pyrquinacridine*,  $C_{23}H_{13}N_3$ , is obtained by distilling the acids with lime. It crystallises from toluene in almost colourless, slender needles, m. p. 265°, and dissolves in concentrated acids, salts being deposited on dilution. The following are described: *hydrochloride*,  $B \cdot 2HCl \cdot 2 \cdot 5H_2O$ ; *hydriodides*,  $B \cdot 3HI$  (possibly, however,  $B \cdot I_3 \cdot HI$ ) and  $B \cdot HI$ ; *nitrates*,  $B \cdot 3HNO_3$  and  $B \cdot HNO_3$ .  
J. C. W.

**The Simplest Rhoduline.** F. KEHRMANN and M. RAMM (*Ber.*, 1918, 51, 385—388).—An account of the preparation and properties of 3:7-diamino-5-methylphenazonium salts.

3:7-Diacetylamino-phenazine is mixed with methyl sulphate (1 mol.) and nitrobenzene at 150°, and the product is treated with hydrochloric acid, whereby a mixture of the chlorides of three methyl derivatives is precipitated. This is repeatedly extracted with hot alcohol, which dissolves small quantities of the chloride of 2:8-diacetylamino-5-methylphenazonium, and the residue is hydrolysed by dissolving in sulphuric acid and cautiously mixing with water. The dark red solution is then rendered alkaline by ammonia and extracted with ether, which dissolves 3-amino-7-methylaminophenazine, when the 3:7-diamino-5-methylphenazine remaining in the red solution may be precipitated in the usual way as the *nitrate*, long, metallic-green needles, *perchlorate* (green solution in concentrated sulphuric acid, becoming violet and then red on dilution), *platinichloride*, or *dichromate*.  
J. C. W.

**Phencyazonium Compounds.** F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, 51, 388—391).—Ehrlich and Benda (*A.*, 1913, i, 904) treated some acridine and pyronine dyes with potassium cyanide, thereby obtaining "leucocyanides," which yielded on oxidation dyes with the same properties as the corresponding azonium salts. For example, 2:8-diamino-10-methylacridine yields 2:8-diamino-5-cyano-10-methylacridine salts (I) which resemble phenylsafranine salts (II).



It appears, therefore, that the  $:C:C:N$  group has about the same

tinctorial influence as the nitrogen atom, and it seemed to be of interest to prepare the chromogen of this type.

This is obtained by oxidising Kaufmann and Albertini's 5-cyano-10-methyldihydroacridine (A., 1909, i, 606), a warm acetic acid solution being merely exposed to the air. The 5-cyano-10-methyl-acridinium salt, or "10-methylphenyazonium" salt, so formed may be converted into the *perchlorate*, which crystallises in yellowish-brown leaflets, and dissolves in sulphuric acid with orange-yellow colour, forming a mono-acid salt only. J. C. W.

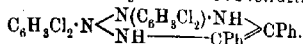
**The Products of the Condensation of 2:4-Dichlorophenylhydrazine with Aldehydes, 1:2-, 1:3-, and 1:4-Diketones and 1:3-Ketocarboxylic Esters, and their Behaviour towards Chlorine.** CARL BÜLOW [with R. HUSS] (*Ber.*, 1918, 51, 399—417).—The author has shown recently that phenylhydrazones of the type  $\text{NHPH}\cdot\text{N}\cdot\text{C}(\text{NHR})\cdot\text{CO}_2\text{Et}$  are decomposed by chlorine in cold alcohol, the phenylhydrazine residue being removed as a diazonium chloride (this vol.; i, 42, 196). It appeared to be of interest, therefore, to examine the action of chlorine on simple phenylhydrazones,  $\text{NHPH}\cdot\text{CHR}$ , and in the sequel it appears that a diazonium salt is always formed if the compound is a genuine phenylhydrazone. In fact, the non-production of a diazonium salt may be taken as strong presumptive evidence that the so-called phenylhydrazone has some other structure.

2:4-Dichlorophenylhydrazine was chosen as a base from which to prepare suitable hydrazones. It may be obtained by boiling ethyl *o*-toluidinoglyoxylate 2:4-dichlorophenylhydrazone with hydrochloric acid (*ibid.*, 197) or from 2:4-dichloroaniline by the usual method (Chattaway and Pearce, T., 1915, 107, 32).

The 2:4-dichlorophenylhydrazone of *o*-chlorobenzaldehyde,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ , crystallises in felted, pale yellow needles, m. p. 168—169°, and forms a yellow solution when chlorine is slowly passed into a suspension in cold alcohol. This solution contains a diazonium salt,  $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{N}_2\text{Cl}$ , for it couples with  $\beta$ -naphthol or  $\alpha$ -naphthylamine, and it yields a substance, m. p. 82—86°, on treatment with water. *m*-Nitrobenzaldehyde-2:4-dichlorophenylhydrazone forms yellow needles, m. p. 207°, and dissolves in cold alcohol when treated with chlorine, the solution almost immediately depositing a substance, m. p. 146—147°, and coupling with  $\beta$ -naphthol to form 2:4-dichlorobenzene-*azo*- $\beta$ -naphthol, m. p. 188—189°. *Salicylaldehyde*-2:4-dichlorophenylhydrazone crystallises in glittering needles, m. p. 148°, and also yields a diazonium salt with chlorine. *Vanillin*-2:4-dichlorophenylhydrazone, m. p. 135°, likewise forms the diazonium salt. These hydrazones dissolve in concentrated sulphuric acid with deepening of colour, but are precipitated with the original tints if the solutions are quickly poured on ice.

Benzil yields a compound which is indifferent to chlorine. It can scarcely be, therefore, the normal "osazone," although it has the same composition, and it is probably 5:6-diphenyl-2:3-di-*o*-

*dichlorophenyl-1:2:3:4-tetrahydro-1:2:3:4-tetrazine*,



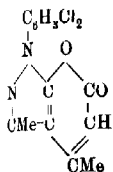
It crystallises in lemon-yellow needles, m. p. 217°.

Similarly, benzoylacetone yields 1-*op-dichlorophenyl-5-phenyl-3-methylpyrazole*,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{N} \begin{array}{c} \text{N}=\text{CMe} \\ \text{CPh} \cdot \text{CH} \end{array}$  in snow-white needles, m. p. 95°, which is attacked by chlorine, but without producing a diazonium salt.

Ethyl diacetosuccinate gives *ethyl 1-*op-dichloroanilino-2:5-dimethylpyrrole-3:4-dicarboxylate**,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{N} \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$  in snow-white needles, m. p. 102°, which dissolves without colour change in sulphuric acid and does not form a diazonium salt.

Ethyl acetoacetate forms "*1-*op-dichlorophenyl-3:4-dimethyl-1:2-pyrazo-6:7-pyrone**" (annexed formula), which crystallises in yellow, rhombic leaflets, m. p. 223°. This is very stable towards acids or dilute alkalis, and, whilst chlorine does attack it, no diazonium salt is formed.

*Acetone 2:4-dichlorophenylhydrazone* is an unstable substance which crystallises in rhombs, m. p. 42°, b. p. 200°/100 mm., and is condensed by zinc chloride at 190° to *5:7-dichloro-2-methylindole*. This forms large, highly refractive, rhombic crystals, m. p. 61°, and gives a deep violet-red coloration when a very minute trace is moistened with concentrated hydrochloric acid.



J. C. W.

**Development of Colours Produced on the Plant Fibre with Diazotisable Dyes.** AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P., 303409, 1917; from *Chem. Zentr.*, 1918, i, 495—496).—The dye, after diazotisation in the usual way, is developed by treatment with an *N*-alkyl derivative of chloro-*m*-phenylenediamine.

4-Chloro-*m*-phenylene-ethylidiamine, colourless crystals, m. p. 53°, can be obtained by nitrating *p*-chloroacetoethylanilide, followed by removal of the acetyl radicle and reduction of the remaining *p*-chloro-*m*-nitroethylaniline. 4-Chloro-*m*-phenylenedimethylidiamine, colourless leaflets, m. p. 80°, is obtainable by nitrating *o*-chlorodimethylaniline and reducing the resultant nitro-compound.

D. F. T.

**Globulin of Buckwheat, *Fagopyrum fagopyrum*.** CARL O. JOHNS and LEWIS H. CHERNOFF (*J. Biol. Chem.*, 1918, **34**, 439—445).—The globulin of buckwheat has the following percentage composition: C 51.69, H 6.90, N 17.44, S 1.16, and O 22.81. It contains about 13% of arginine, 0.6% of histidine, 7.9% of lysine, and 1% of cysteine, besides a small amount of tryptophan.

H. W. B.

**Stizolobin, the Globulin of the Chinese Velvet Bean, *Stizolobium niveum*.** CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1918, **34**, 429—438).—The new globulin, *stizolobin*, is the chief protein in the Chinese velvet bean. It has the following percentage composition: C 53.03, H 7.05, N 16.33, S 0.65, and O 22.94; and it contains about 1.15% of cysteine, 6.7% of arginine, 2.4% of histidine, and 8.5% of lysine. Tryptophan is also present in stizolobin. H. W. B.

**The Swelling of Protein Colloids.** LAURENCE J. HENDERSON and EDWIN J. COHN (*J. Amer. Chem. Soc.*, 1918, **40**, 857—861).—In reference to the investigations of Fischer and his co-workers (this vol., i, 129, 130, 131), it is stated that careful consideration of the experimental results fails to support the conclusions which have been drawn (see following abstract). D. F. T.

**The Colloidal-Chemical Theory of Water Absorption by Protoplasm.** MARTIN H. FISCHER (*J. Amer. Chem. Soc.*, 1918, **40**, 862—867).—A reply to Henderson and Cohn (preceding abstract). D. F. T.

**Swelling of Protein Colloids.** L. J. HENDERSON (*J. Amer. Chem. Soc.*, 1918, **40**, 867—868).—A reply to Fischer (preceding abstract). D. F. T.

**Preparation of Strong Solutions of Hæmoglobin and of Colour Filters of Hæmoglobin Compounds.** H. HARTRIDGE (*J. Physiol.*, 1917, **51**, 252—258).—Solutions of hæmoglobin containing up to 48% were obtained by dialysing centrifuged sheep's corpuscles in a collodion tube against flowing distilled water at 0° for a week or less in Dewar vessels. By mixing with warm gelatin solutions, colour filters of oxy- and carbonmonoxide-hæmoglobin were prepared, but they were not permanent. G. B.

**Hæmin Crystals and their Production.** ZDZISLAW ZAWAL-KIEWICZ (*Pharm. Post.*, 1918, **51**, 45; from *Chem. Zentr.*, 1918, i, 540—541).—Teichmann's reaction is obtained most easily by placing a small quantity of the substance under examination on an objective glass with a drop of *N*/10-hydrochloric acid; this is then very carefully dried above a small flame, the residue moistened with 2—3 drops of concentrated acetic acid and a cover glass placed over the mixture. The mixture is again carefully warmed for about a minute, any acid lost by evaporation being replaced by another drop. When the end of the reaction is indicated by a reddish-brown colour, the remainder of the acid is allowed to evaporate, one or two drops of glycerol are introduced under the cover glass, and the characteristic crystals of hæmatin chloride are examined under the microscope. Ammonium chloride can be used satisfactorily in place of sodium chloride. D. F. T.

**Crystalline Nucleic Acids.** S. J. THANNHAUSER and G. DORFMÜLLER (*Ber.*, 1918, **51**, 467—468).—Triphosphonucleic acid

(this vol., i, 47) has been partially hydrolysed to *cytidine-phosphoric acid*,  $C_9H_{14}O_8N_3P$ , rosettes of stout monoclinic-sphenoidal crystals, m. p.  $227^\circ$  (decomp.) (*di-brucine* salt, m. p.  $180-182^\circ$ ), and *guanosine-adenosine-phosphoric acid*,  $C_{20}H_{28}O_{13}N_{10}P_2$ , stout, unsymmetrical triclinic crystals, m. p.  $208^\circ$  (decomp.) (*tetra-brucine* salt, m. p.  $170^\circ$ ). Details of the process employed will be given in a subsequent, comprehensive communication.

J. C. W.

**Stoichiometrical Character of the Action of Normal Salts on the Swelling of Gelatin.** JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 77-95. Compare this vol., i, 240; and Fenn, this vol., i, 318, 319).—The method previously described for the estimation of the effect of normal salts on the swelling of powdered gelatin has been applied to sodium gelatinate prepared by the action of  $M/100$ -sodium hydroxide, and to gelatin chloride prepared by the action of  $M/100$ -hydrochloric acid, on gelatin. It is found that the additional swelling of gelatin chloride is inhibited in solutions of normal salts with univalent cations and anions (type sodium chloride) in concentrations above  $M/64$ , and by salts with bivalent cations and univalent anions (type calcium chloride) in concentrations exactly half as high, namely, above  $M/128$ , no matter what the nature of cation or anion. Salts with bivalent anions (type sodium sulphate) have a limiting concentration of a much lower order, namely,  $M/512$ . In the case of sodium gelatinate, the limiting molecular concentration at which swelling is inhibited is twice as great for salts containing univalent anions and cations (such as sodium chloride) as for salts containing bivalent anions and univalent cations (such as sodium sulphate), whilst salts with bivalent cations (such as calcium chloride) have much lower limiting molecular concentration. Further, the additional swelling of gelatin, treated with  $M/8$ - or  $M/4$ -sodium chloride solution, is inhibited by normal salts in exactly the same way and at the same concentrations as sodium gelatinate. The normal salts, therefore, produce the same type of compounds with gelatin as the bases, namely, metal gelatinates which dissociate into a positive metal and a negative gelatin ion. These facts show that the limiting concentration of normal salts for the additional swelling is, within the restrictions mentioned, independent of the nature of the anion and cation of the salt, and this method could be used to calculate roughly the molecular concentration of the salt used.

When normal salts act on sodium gelatinate, apparently only the cation of the salt combines with the gelatin; and when normal salts react with gelatin chloride, only the anion will combine with gelatin, but not the cation. The experiments also show that gelatin salts with univalent anion or cation, such as gelatin chloride or sodium gelatinate, are capable of additional swelling, whilst salts of gelatin with bivalent ions are not. It is suggested that the swelling is due to electrolytic dissociation, which only occurs to a small extent in the case of gelatin salts with bivalent ions. It is evident that antagonistic salt action may be expected when

gelatin salts containing univalent ions are transformed into gelatin salts with bivalent ions.

H. W. B.

**Influence of Normal Salts on the Viscosity of Gelatin Solutions.** JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 395—413. Compare preceding abstract).—After gelatin has been treated with  $M/8$ - or  $M/16$ -solutions of normal salts with univalent cations, and the excess of salt then washed away, its viscosity is found to have increased. The viscosity is estimated by dissolving an amount of the treated gelatin, corresponding with 1 gram of the dry material, in water and comparing the rate of outflow through a viscometer at  $24^{\circ}$  with that of a solution containing 1 gram of washed gelatin powder in the same volume (100 c.c.) of water. The effect on the viscosity is stoichiometrical, in so far that all normal salts with univalent cations produce the same increase in the viscosity of the gelatin solution, so long as the concentration of cation is the same, regardless of the nature and valency of the anion. Salts with bivalent cations do not produce any increase in the viscosity of gelatin.

The action of salts on the viscosity of sodium gelatin is similar to that observed in the case of gelatin, but with gelatin chloride (gelatin previously treated with  $N/100$ -hydrochloric acid) salts with bivalent anions lower the viscosity of such treated gelatin, salts with univalent anions have the opposite effect, whilst the influence of the cations is imperceptible.

These results indicate that the viscosity of a gelatin solution is influenced chiefly, if not exclusively, by only one of the two ions of the normal salt, namely, the one with an electrical charge opposite to that of the protein. Ordinary gelatin has acidic properties, and its viscosity is influenced, therefore, only by cations. The same position is occupied by sodium gelatin, but gelatin chloride, yielding a positive gelatin ion, is affected only by anions. Support is also afforded by these results to the hypothesis that gelatinates with univalent cations are highly dissociable, whilst those with bivalent cations are not.

H. W. B.

**Effects of Electrolysis on Gelatin and their Biological Significance. III. Effects of Mixtures of Salts on the Precipitation of Gelatin by Alcohol. Antagonism.** W. O. FENN (*J. Biol. Chem.*, 1918, **34**, 141—160. Compare this vol. i, 240; and Loeb, preceding abstract).—By the method previously described, it is shown that salts (like sodium chloride) with univalent anions and cations decrease the effect of salts with bi- or ter-valent anions or cations on the precipitability of gelatin by alcohol, whilst salts with bi- or ter-valent cations antagonise those with bi- or ter-valent anions. Small concentrations of salts with bivalent cations (like calcium chloride) decrease the effect of sodium chloride on gelatin, whilst small concentrations of salts with bi- or ter-valent anions (like sodium sulphate) increase it. A pair of salts with bivalent cations or a pair with univalent anions and cations are not antagonistic in their effects.

H. W. B.

**Effects of Electrolytes on Gelatin and their Biological Significance. IV. Precipitation of Gelatin by Mixtures of Salts.** W. O. FENN (*J. Biol. Chem.*, 1918, **34**, 415—428. Compare preceding abstracts).—The effect of a mixture of salts on the precipitability of gelatin depends on the nature of the ions which are present. The experiments are performed by dissolving the gelatin in acid, alkali, or a normal salt, and estimating the amount of sodium chloride or sulphate which must be added in the solid form just to cause its precipitation. Acids, and salts in which the effect of the cation predominates, assist the precipitation of gelatin by sodium chloride, whilst alkalis, and salts with predominant anions, hinder it. When sodium sulphate is substituted for sodium chloride, the precipitation of the gelatin is hindered by small, and assisted by higher, concentrations of alkali. H. W. B.

**The Variability in the Activity of Ptyalin.** F. DE BRUYNE (*Arch. néerland. physiol.*, 1918, **2**, 358—363).—Some observations indicating a periodicity in the activity of ptyalin when kept at 35°. S. B. S.

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## Physiological Chemistry.

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**Respiratory Metabolism and the Question as to the Formation of Sugar from Proteins and their Degradation Products.** JOSÉ M. DE CORRAL (*Biochem. Zeitsch.*, 1918, **86**, 176—222).—It has been shown that the administration of Witte's peptone to a dog renders the liver practically free from glycogen. The effect of this administration on the respiratory quotient has been investigated, and also the effect of adding protein and amino-acid diets after peptone treatment. The Jacquet apparatus was employed for measurement of the gaseous exchanges. After eight days' starvation, the respiratory quotient for dogs sinks to 0.682, which is less than that after ingestion of fat. Practically the same low respiratory quotient is obtained after an interval of some hours after the last treatment, when the animal has had Witte's peptone administered to it for two days. When a carbohydrate diet is given, it is possible to determine the formation of glycogen by ascertaining the respiratory quotient seventeen or eighteen hours after the last ingestion. That the capacity for forming glycogen from carbohydrates after administration of peptone is diminished can be ascertained, even after an interval of twenty-four hours. But although diminished, it still exists, as is shown by comparing the value of the respiratory quotient with that obtained after administration of carbohydrates during starvation. If fats exclusively are administered after two days' treatment with peptone, the respiratory quotient in a following period



of starvation is the same as that after peptone action. If, after peptone treatment, amino-acids or proteins are administered, carbohydrates are formed, for the respiratory quotient in the following period of starvation indicates combustion of carbohydrates. Such a formation of carbohydrates from amino-acids or meat only appears to take place, however, when carbohydrates are wanting in the organism.

S. B. S.

**The Wanderings of the Ions in Serum and Blood under the Influence of Carbon Dioxide, Acid, and Alkali.** H. J. HAMBURGER (*Biochem. Zeitsch.*, 1918, **86**, 309—324).—The author, using an ultra-filtration method, is able to confirm the statement of Rona and György, that when carbon dioxide acts on the serum, the chlorine passes into a non-diffusible form, by combining with the proteins. The same happens after addition to the serum of very small amounts of sulphuric acid and of larger amounts of acetic acid.  $\text{SO}_4$  also passes into a non-diffusible form after treatment of the serum with hydrochloric acid. When carbon dioxide acts on blood, it is possible to ascertain that not only does  $\text{SO}_4$  attach itself in non-diffusible form to the serum proteins, but that it also goes into the corpuscles. The same phenomena take place after addition to blood of minute amounts of hydrochloric acid. The reverse effect to that produced by acids is observed after addition of small amounts of potassium hydroxide, in that  $\text{Cl}$  and  $\text{SO}_4$  are set free from combination with the proteins and pass into a diffusible form.

S. B. S.

**Can the Amount of Combination of Carbon Dioxide with Blood-serum be regarded as a Measure of the Reaction of the Blood?** K. A. HASSELBALCH and E. J. WARBURG (*Biochem. Zeitsch.*, 1918, **86**, 410—420).—The carbon dioxide tension, under which the blood is centrifuged for separation of the serum, is of great influence. By high carbon dioxide tension during centrifugalisation, the curve representing the relationship between carbon dioxide tension and carbon dioxide bound to the serum is shifted upwards, whereas by lower tension during centrifugalisation, it is shifted downwards. For this reason, it is not possible to draw correct conclusions as to acidosis and the reaction of the blood by measuring the capacity of the serum to combine with carbon dioxide, unless account is taken of the tension of the carbon dioxide prevailing during the preparation of the serum from the blood. It may be recalled that the carbon dioxide tension influences also the distribution of  $\text{Cl}$  and other ions between the serum and corpuscles (Hamburger).

S. B. S.

**The Presence of Phosphates in Human Blood-serum.** V. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **86**, 395—409. Compare A. 1917, i, 520; this vol., i, 50, 203).—An analysis of the various forms of phosphorus in the serum in six pathological cases.

S. B. S.

**The Presence of Invertase in Serum.** G. H. BOISSEVAIN (*Arch. néerland. physiol.*, 1918, 2, 415—419).—The discordant results of various observers as regards the presence of invertase in the serum after injection of sucrose are discussed. It is shown that the leucocytes contain invertase, and it is suggested that the presence in the serum after injection of various sugars in solution is due to the injury of the leucocytes and the setting free of the ferment; in fact, an invertase can be detected in the serum after injection of water, or the formation of a clot in the veins by introduction of a silk thread. The leucocytes used in the experiments were obtained from an aseptic abscess produced by terebenthene. S. B. S.

**Antigens. XII. The Relationship between Serological Specificity and Chemical Structure. (Preparation of Antigens with Specific Groups of known Chemical Structures).** KARL LANDSTEINER and HANS LAMPL (*Biochem. Zeitsch.*, 1918, 86, 343—394).—A series of antigens was made by combining horse serum with the diazo-derivatives obtained from the following "azo-components": aniline, *o*-, *m*-, and *p*-aminobenzoic acids, *o*-, *m*-, and *p*-aminobenzenesulphonic acids, *p*-aminophenyl-arsinic acid, and a number of chloro-, bromo-, and nitro-*o*-substitution products of these substances, *o*-, *m*-, and *p*-aminocinnamic acids, naphthionic acid, and aminoazobenzenedisulphonic acid. The method of preparing solutions containing serum proteins coupled with these various diazo-derivatives is described. The antigens were then injected into rabbits until active immune sera were obtained. The precipitin reaction of the various immune sera towards native horse sera differed. The reaction of the immune sera towards the various antigens (diazo-proteins) prepared from horse serum, egg-albumin, and in a few cases edestin, was also investigated. Altogether 23 kinds of immune sera were prepared, and their action on 33 azoproteins was investigated. Of these, only 6 were completely specific, acting only on the homologous antigens containing the same azo-components. Of the antigens, 15 acted only with one immune serum. The other immune sera and antigens showed a broader sphere of action. The results are tabulated by the author, who summarises the relationship of the various antigens to one another and the relationship of the chemical structure of the azo-components and serological action. The possibility of distinguishing chemical groups by serological reactions is suggested. S. B. S.

**Calcium and Magnesium Metabolism. IV. Experiments on Man.** MAURICE H. GIVENS (*J. Biol. Chem.*, 1918, 34, 119—130. Compare A., 1917, 1, 603).—The daily urinary excretion of calcium and magnesium of nine healthy adults on a diet of natural foods containing more magnesium than calcium ranged from 0.05 to 0.24 gram of calcium and from 0.03 to 0.15 gram of magnesium, whilst on a diet having more calcium than magnesium the limits

were 0.12 to 0.47 gram of calcium and 0.05 to 0.23 gram of magnesium. In general, although not always, more calcium than magnesium is excreted in the urine. The urinary output of both calcium and magnesium is increased by consumption of milk; calcium lactate always increases the urinary excretion of calcium, although not to such an extent as is effected by milk; magnesium lactate does not seem to produce any greater elimination of magnesium in the urine. The results obtained do not allow of any simple relationship being established between urinary excretion of calcium and body-weight.

H. W. B.

**Carbohydrate Metabolism. I. Elimination of Sugar in the Urine of the Normal Dog.** STANLEY R. BENEDICT and EMIL OSTERBERG [with CECIL DUDLEY] (*J. Biol. Chem.*, 1918, **34**, 209—216).—By means of a new method for estimating traces of sugar in urine (this vol., ii, 247), the authors are able to record the changes in the hourly excretion of sugar by a normal dog. The amount of sugar eliminated is independent of the volume of urine secreted. The percentage of sugar varies greatly; in one dog it ranged from 0.021 to 0.36%. The amount of sugar excreted per hour gradually rises after a meal, reaches a maximum in about five hours, and then falls to normal. The urine almost invariably contains some kind of sugar, but occasionally during the periods of minimum elimination, fermentable sugar (dextrose) disappears entirely from the urine. During the period of maximum sugar elimination, the reaction of the urine approaches neutrality, and in some cases becomes alkaline to litmus. The twenty-four hours' sample was invariably acid. The discussion of the bearing of these points on views as to carbohydrate metabolism is reserved for a future paper.

H. W. B.

**Carbohydrate Metabolism. II. Urinary Sugar Excretion in Two Normal Men.** STANLEY R. BENEDICT, EMIL OSTERBERG, and ISAAC NEUWIRTH (*J. Biol. Chem.*, 1918, **34**, 217—262. Compare preceding abstract).—The results show that sugar is always present in normal human urine. Feeding with either meat or a carbohydrate diet causes an increase in the elimination of sugar. Glycosuria is therefore a physiological condition, and the normal organism can be said to be diabetic. The authors propose to abandon the use of the word "glycosuria," and suggest the term "glycuresis" to denote an increase of sugar in the urine. Glycuresis occurs after the ingestion of food, the percentage of sugar in the urine rising after a meal from about 0.05 to 0.3 or sometimes to as much as 0.6. A certain degree of tolerance for dextrose is shown in that, after the ingestion of 20 to 50 grams of dextrose, the resulting glycuresis is not greater than is observed after an ordinary meal. Yet the addition of 20 grams of dextrose to an ordinary meal may lead to a relatively great output of sugar in the urine, indicating a profound disturbance in carbohydrate metabolism. The total amount of sugar eliminated in the urine by a normal person is about 1 to 1.5 grams daily, and in persons

with a tendency to diabetes this maximum is not only exceeded, but the ratio of unfermentable to fermentable sugar in the urine becomes changed.

H. W. B.

**Inorganic Elements in Nutrition.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 131—140).—Full description of work previously published (this vol., i, 277).

H. W. B.

**Nutritive Factors in Animal Tissues. II.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 17—27. Compare this vol., i, 140).—Besides the liver, the heart, kidney, or brain of the pig contains sufficient water-soluble vitamine to effect rapid growth in the rat when constituting the sole source of protein and water-soluble vitamine in the food. In some cases, normal growth occurs also without the addition of any source of fat-soluble vitamine other than that contained in the tissue itself. These tissues are therefore better foods than dried beef (compare Cooper, A., 1914, i, 777, and Osborne and Mendel, *loc. cit.*). They can be dried and heated for several hours at 90° without any loss of water-soluble vitamine occurring. The oil expressed from liver tissue is rich in fat-soluble vitamine, and it effectively cures or prevents the nutritive decline and the pathological manifestations which are the characteristic outcome of feeding with a diet otherwise devoid of fat-soluble vitamine.

H. W. B.

**The Nature of the Constituent of Intestinal Extracts which Exerts a Stimulating Influence on the Gastro-intestinal Movements.** J. W. LE HEUX (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 805—811). The presence of this constituent was first demonstrated by Wieland. The author describes experiments for its isolation, and draws the conclusion that it is most probably choline. Its physiological activity is markedly increased by acetylation.

S. B. S.

**Quantity of Metal Fixed by Organic Extracts and Proteins. II. Catalytic Power of Egg-albumin treated with Metallic Powders.** S. REBELLO-ALVES and A. BENEDICENTI (*Arch. farm. sper. sci. off.*, 1917, **24**, 79—96, 150—156; from *Physiol. Abstr.*, 1918, **3**, 100).—Powdered copper and cobalt are fixed in varying proportions by different organs; liver, owing to its more rapid autolysis, fixes most.

The catalytic power of egg-albumin towards hydrogen peroxide is not increased by heating it with powdered quartz, but is increased five or six times by cobalt powder. Nickel, iron, and copper do not increase catalysis, and lead and antimony diminish it.

S. B. S.

**Suprarenal Glands in Relation to Carbohydrate Metabolism. I. Influence of Repetition of Adrenaline Injection on the Intensity of Glycosuria and Hyperglycæmia and the Glycogen Content of the Liver. II. Influence of Adrenalectomy on the Glycogenetic Power of the Liver. III. Adrenaline Content of the Suprarenal Glands in Various Experimental Conditions.** SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **34**, 269—285, 287—297, 299—319).—Daily repetition of subcutaneous injection of adrenaline is followed on each occasion by the excretion of about the same quantity of sugar in the urine so long as the animals (rabbits) are well fed. When the animals are allowed to fast, the daily sugar excretion rapidly diminishes until only a slight glycosuria is produced. The hyperglycæmia produced by daily adrenaline injections remains practically constant, no matter whether the animal is fasting or well fed. The reason of the failure of the hyperglycæmia caused by the injection of adrenaline into fasting animals to produce the typical glycosuria is not elucidated. Injection of adrenaline into fasting rabbits leads to a storage of glycogen in the liver. A combination of fasting and adrenaline injections does not therefore render the liver of an animal free from glycogen.

Rats after adrenalectomy still retain the power to form glycogen from carbohydrates in the liver; adrenaline does not exert a controlling action on the glycogenetic function of the liver.

The amount of adrenaline in the suprarenal gland after removal from the body gradually diminishes unless the gland is kept in an oxygen-free medium. The adrenaline content of the gland in the living rabbit is not altered by fasting, by repeated injections of adrenaline, or by injection of a single large dose of this substance. Removal of one gland is partly compensated for by growth of the companion gland, resulting in an increase in the absolute amount of adrenaline in the gland, although, owing to the relatively greater growth of the glandular tissue, the percentage of adrenaline in the companion gland is reduced.

H. W. B.

**Estimation of Various Forms of Nitrogen in Raw Beef, including the Products of Hydrolysis of some of the Proteins. I. Hexone Bases of some Proteins of Beef. II. Bromination of the Hydrolysates of some Proteins of Beef.** WALTER E. THRUN and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1918, **34**, 343—353, 355—362). Compare Trowbridge and Grindley, *A.*, 1906, ii, 374).—The proteins of beef which are insoluble in cold water, yield on hydrolysis less humin, ammonia, histidine, and more arginine nitrogen than the coagulated water-soluble proteins. Since the former represent the stroma and the latter the plasma of the muscle fibres, it appears that these components of the cell are composed of essentially different proteins. The comparison of the analyses of the muscular tissues of a new-born calf and of a five-year-old steer indicates that during growth the insoluble proteins probably change in composition.

A method is described for estimating histidine in proteins by

hydrolysis followed by bromination. After deducting the amount of bromine absorbed by cysteine and allowing for the solubility of histidine in phosphotungstic acid, figures are obtained which tally closely with those afforded by Van Slyke's method (A., 1911, ii, 944). Under the conditions described, a molecule of cysteine absorbs about ten atoms of bromine, whilst a molecule of histidine absorbs two.

H. W. B.

**The Skin Secretion of Frogs.** FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1917, 81, 319-382). The secretion is best obtained by electrical stimulation of washed frogs, and consists of coagulable protein, mucin, albumoses, peptones, amino-acids (7% of leucine), purine bases, cholesterol and its esters. The dried secretion kills tadpoles and small fishes in a 1:80,000 solution; 6-12 mg. per kilo. intravenously kills rabbits. The dried secretion has a strong local irritant action on the skin; the active substance resembles the saponins in its chemical and pharmacological properties, and is quite distinct from the heart poison of the toad's skin. It could not be obtained pure, but gives Liebermann's cholesterol reaction and seems to be a lactone.

G. B.

**The Excretion of Saponins in the Urine, and their Action on the Blood after Internal Administration.** JOSEF FIEGER (*Biochem. Zeitsch.*, 1918, 86, 244-297). Sapindus saponin, after administration to dogs, is partly excreted in the unchanged form in the urine, and can be detected by its hæmolytic action. The sapogenin can also be isolated from the urine after hydrolysis with sulphuric acid; this substance exerts also a hæmolytic action. The detection of the guaiacum saponin in the urine is most difficult, as it is not hæmolytic. The author shows, however, that it yields on hydrolysis two sapogenins, the mixture of which is strongly hæmolytic. The urine of an animal to which the saponin had been administered is not hæmolytic, but it exerts a hæmolytic action after hydrolysis. The saponin is therefore excreted in the urine unchanged. In an experiment with quillaja saponin, this substance could not be detected in the urine; in this case, however, the experiment had been carried out on an animal to which other saponins had been previously administered, and reasons are given for supposing the animal had acquired a general tolerance to the group of saponins, and had degraded the quillaja saponin in the intestine, excreting the sapogenin in the fæces. In the case of a second dog to which the saponin was administered, small amounts were found in the urine. In the case of all three saponins, a marked excretion of bile pigments in the blood took place, which is taken as evidence of the resorption of these substances. They also exerted a temporary diuretic action.

S. B. S.

**The Excretion of Saponin in the Fæces.** HANS BÄCK (*Biochem. Zeitsch.*, 1918, 86, 223-242).—Sapindus and quillaja saponins were administered to hens and dogs. They cause irritation of the alimentary tract, and undergo hydrolysis either by

enzymes or by microbes. The saponinins are excreted with the faeces, and their presence was detected by their hæmolytic action on the corpuscles of various species. From the sapindus saponin apparently two saponinins are obtained in the faeces, one of which is soluble in ethyl acetate and is strongly hæmolytic, whilst the other is insoluble and not hæmolytic. From quillaja saponin, two saponinins also appear to be formed, one soluble in ethyl acetate and strongly hæmolytic, the other insoluble in this reagent, but weakly hæmolytic.

S. B. S.

**Cæsium Ions and Cardiac Action.** H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 773-778).—The light radioactive metals and the allied cæsium, as well as the heavy radioactive metals uranium, thorium, niton, and radium, sustain the contractility of the isolated frog's heart when the ventricle is pulsating on its own activity. The author gives the effectual doses of these for summer frogs. There is a biological antagonism between potassium, cæsium, and rubidium, on the one hand, and uranium, thorium emanation, and niton, on the other. Probably cæsium emits  $\beta$ -rays of low penetrating power on which its effect, similar to that of potassium and rubidium, depends.

S. B. S.

**Distribution and Elimination of Zinc and Tin in the Body.** WILLIAM SALANT, J. B. RIEGER, and E. L. P. TREUTHARDT (*J. Biol. Chem.*, 1918, **34**, 463-470).—After the administration of zinc salts to cats or rabbits by the mouth, or by subcutaneous or intravenous injections, the metal is eliminated almost entirely in the faeces. Tin salts are similarly dealt with, except that a significant proportion passes off in the urine. Storage of both metals occurs in the liver, skin, and bones.

H. W. B.

**Production of Glycosuria by Zinc Salts.** WILLIAM SALANT and LOUIS ELSBERG WISE (*J. Biol. Chem.*, 1918, **34**, 447-462).—The intravenous injection of zinc malate into rabbits produces slight hyperglycemia and glycosuria. Glycosuria is also caused by subcutaneous injections and by the administration of the zinc malate or acetate with the food, but much larger doses are required. The amount of sugar in the urine after the injection usually reaches about 0.35 per cent. Albuminuria accompanies the glycosuria and is sometimes very marked.

H. W. B.

**Dichloroethylene as a Narcotic.** HERMANN WITTGENSTEIN (*Arch. exp. Path. Pharm.*, 1918, **83**, 235-247).—An atmosphere containing about 1% by volume of dichloroethylene causes deep narcosis in various mammals, but, unlike chloroform, it does not depress the heart and blood vessels. It has been successfully tried on man in a few cases.

G. B.

**The Taking up of Ethyl Alcohol by the Lungs.** A. LOEWY and R. VON DER HEIDE (*Biochem. Zeitsch.*, 1918, **86**, 125-175).—A detailed investigation of the amounts of ethyl alcohol taken up

from the air by rats and guinea-pigs and of the amounts remaining in the bodies and burnt. As compared with methyl alcohol, the amounts of ethyl alcohol stored in the body are small. The amount stored per millimetre tension of alcohol vapour in the air is smaller the greater the tension. The combustion of ethyl alcohol is greater than that of methyl alcohol, and this accounts for the greater quantities of the latter found stored in the body. The conclusion is drawn that ethyl alcohol is, generally, more toxic than methyl alcohol. A few experiments on man are also described.

S. B. S.

**Gossypol, the Toxic Substance in Cotton Seed.** W. A. WITHERS and FRANK E. CARRUTH (*J. Agric. Research*, 1918, **12**, 83—102. Compare Carruth, this vol., i, 266).—Cotton-seed meal is much less toxic than raw cotton seed, probably owing to the oxidation of gossypol during cooking. Feeding experiments with rats, rabbits, and pigs are described, details of which are given in *J. Soc. Chem. Ind.*, 1918, 164A.

W. G.

**Metabolic Changes Induced by Administration of Guanidine Bases. II. Influence of Guanidine on Urinary Ammonia and Acid Excretion. III. Relation between the Tetanoid Symptoms of Guanidine Administration and the Condition of Acidosis. IV. Influence of the Administration of Calcium on the Sugar Content of the Blood in Rabbits with Guanidine Hypoglycæmia.** C. K. WATANABE (*J. Biol. Chem.*, 1918, **34**, 51—63, 65—72, 73—76. Compare this vol., i, 205).—The subcutaneous injection of guanidine hydrochloride into a rabbit is followed immediately by a diminished excretion of nitrogen in the urine. The ammonia eliminated in the urine is increased, however, so that the ratio, ammonia/total nitrogen, is greatly increased. There is a fall in the hydrogen ion concentration, and the urine may become neutral or alkaline.

The effect of the injection on the blood is to produce a marked increase in its hydrogen ion concentration and a corresponding decrease in the alkaline reserve, specially noticeable after the manifestation of the symptoms of tetany. It appears, therefore, that the excretion of the excess of ammonia in the urine in tetany is the result of the operation of a protective mechanism by means of which the liver seeks to neutralise the acid produced by the excessive muscular activity (compare Carlson and Jacobson, A., 1910, ii, 324).

All the toxic symptoms following parathyroidectomy are paralleled by those produced by the injection of guanidine into the system. The hypoglycæmia manifested after thyreoparathyroidectomy is also produced by the administration of guanidine (*loc. cit.*), but it is now shown that neither the tetany nor the hypoglycæmia resulting from guanidine injections can be removed by treatment with calcium lactate, which has been shown to abolish these symptoms when produced by operative procedures (compare Underhill and Blatherwick, A., 1914, i, 1184).

H. W. B.



**The Fate of Quinine in the Organism.** HEINZ HARTMANN and LORO ZILA (*Arch. exp. Path. Pharm.*, 1918, **83**, 221—234).—A gravimetric method of estimation in urine is described (precipitation as tannate, decomposition of the latter, extraction from water with ether), and a method, based on the fluorescence, for estimation in blood (compare Ramsden and Lipkin, this vol., ii, 251). At most, 40% of administered quinine is excreted in urine and faeces; the rest is not deposited in the organs, and must therefore have been destroyed. After intravenous injection, the amount in the blood sinks rapidly, then more slowly, to zero (eight hours after 0.5 gram), but oral administration gives a lower, more constant quinine level, which is retained for about twenty-four hours. G. B.

**Physiological Behaviour of Raffinose. II.** SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **34**, 321—333. Compare Kuriyama and Mendel, A., 1917, i, 611).—Raffinase is present in mung bean (*Phaseolus aureus*), cotton seed, and soja bean. It can also be extracted from rabbits' faeces. Raffinase (from yeast) is readily destroyed by the gastric juice, but when yeast is fed to an animal, a portion of the raffinase escapes destruction and passes into the excreta. H. W. B.

## Chemistry of Vegetable Physiology and Agriculture.

**The Formation of Ferments. VI.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **86**, 329—336. Compare A., 1917, i, 305, 430, 528).—Leucine promotes the urease fermentation in the case of *Bacillus coli*, but it inhibits the sugar-fermenting action of the same bacterium. The significance of certain fragments of the protein molecule for the formation of ferments, and the general physiological significance of proteins for growth, are discussed by the author. S. B. S.

**Influence of Nitrates on Nitrogen-assimilating Bacteria.** T. L. HILLS (*J. Agric. Research*, 1918, **12**, 183—230).—A great increase in the number of azotobacter in sterilised soil was produced by the application of small quantities (up to 0.1%) of potassium, sodium, or calcium nitrate, but ammonium nitrate was much less effective, and higher concentrations of all the nitrates were not so favourable to the growth of the organism. There was also an increase in the total nitrogen in the soil, but this increase was not commensurate with the increase in the number of azotobacter present. On agar films, the results were somewhat different, calcium nitrate causing a decrease in the amount of nitrogen fixed.

All three nitrates caused an increase in the number and size of the volutin bodies in the azotobacter cells and a marked pigmentation. The number of *Bacillus radiculicola* in sterilised soil was increased by the application of small quantities of the three nitrates, and, although this increase was less marked than in the case of azotobacter, the *B. radiculicola* appeared to be more resistant to higher nitrate concentrations. Unlike the azotobacter, *B. radiculicola* does not reduce nitrate to nitrite under aerobic conditions. The presence of large amounts of potassium, sodium, and calcium nitrates proved detrimental to the formation of nodules on alfalfa.

W. G.

**Presence of a Growth-producing Substance in Cultures of Typhoid Bacilli.** AUGUST J. P. PACINI and DOROTHY WRIGHT RUSSELL (*J. Biol. Chem.*, 1918, **34**, 43—49).—It has long been recognised that in certain infectious diseases growth is induced, apparently, by the infection. In typhoid fever, for example, the patient may grow from one to even several inches in height. It is now shown that the fat- and protein-free extract of typhoid bacilli contains a vitamine which when added to the food causes rapid growth of rats on a diet on which otherwise they gradually lose weight and die. The extract gives the blue coloration with Folin's uric acid reagent, which is given by vitamine-containing extracts prepared from yeast and other sources. The authors indicate the bearing of these results on the question of a more scientific method of feeding in these cases.

H. W. B.

**The Preparation of Phosphoric Acid Esters of Carbohydrates (Zymophosphate) by Living Yeasts.** HANS EULER (*Biochem. Zeitsch.*, 1918, **86**, 337—342).—Neuberg has found that yeast in presence of toluene could only bring about an esterification of 7—8% of added phosphate, whereas the author found that it could bring about a complete conversion into the ester. Attention is now directed to the facts (*a*) that excess of toluene acts toxically and inhibits the zymophosphate formation, although small amounts are necessary to bring this about, and (*b*) not all yeasts are capable of zymophosphate formation; two out of eleven bottom beer yeasts investigated by the author gave negative results. The author confirms Harden and Young in showing that dihydroxyacetone can only give rise to a small amount of zymophosphate.

S. B. S.

**The Influence which the Plant Function of Yeast Exercises on the Yield of Alcohol; new Interpretation of Ferment Power.** L. LINDET (*Compt. rend.*, 1918, **166**, 910—913).—An examination of the relative effects of the plant function and the zymase function of yeast during alcoholic fermentation. The author has studied the effect of varying the nutritive value of the bouillon, the concentration of the sugar solution, the vigour of the yeast, the temperature, the thickness of sowing, and the origin of the yeast on the yield of alcohol. The ferment power

must be considered as the sum of the plant power, tending to consumption of sugar, and the zymase power producing the alcohol. These two powers are higher as the crop of yeast is less abundant and the fermentation is prolonged. Except in the case of temperature variation, the weight of sugar utilised to produce a given weight of yeast is independent of the conditions. [See, further *J. Soc. Chem. Ind.*, July.] W. G.

**Precipitation of Proteins by Narcotics.** OTTO MEYERHOF (*Biochem. Zeitsch.*, 1918, **86**, 325—328).—Freundlich and Rona (*A.*, 1917, ii, 365) have explained the sensitisation of colloids to precipitating salts by the action of narcotics. The same explanation applies to the following phenomena, observed with Lebedev's maceration juice of yeast. The original juice is readily precipitated on addition of 6% ethyl urethane. The residue from ultra-filtration is not so precipitated, but precipitation readily takes place when the ultra-filtrate is added to it. The combined action of salts and narcotics is necessary for precipitation. S. B. S.

**Growth of *Aspergillus glaucus* under the influence of Large Quantities of Potassium Nitrate.** H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 599—602).—A series of tables indicating the marked influence exerted by potassium nitrate on the rapidity of growth of *Aspergillus glaucus*. A. J. W.

**Acids Produced by *Mucor Boudard*.** BETTINGER and DELAVALLE (*Bull. Assoc. Chim. Sucr. Dest.*, 1917, **35**, 13—15. Compare *J. Soc. Chem. Ind.*, 1918, 219A, 345A).—*Mucor Boudard* (employed industrially for the saccharification of distillery mashes), cultivated in sugared extract of malt-combs, yields succinic acid as sole non-volatile acid, and a much smaller proportion of acetic acid. The production of acid is favoured by aeration, high sugar-content of the medium, and relatively low temperatures of culture. Ether extracts about 21% of the dry substance of the plant grown under these conditions. J. H. I.

**The Formation of Soluble Starch by Moulds and the Question of the Synthesis of Proteins by these Organisms.** FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1918, **86**, 110—124).—In continuation of his investigations on the formation of soluble starch (*A.*, 1917, i, 370, 503), the author now shows that quinic acid can serve as a source of carbon. In presence of asparagine, the percentage of the acid must be more than 6%, but in the presence of ammonium sulphate, 3.6% of quinic acid is sufficient, as acid is necessary for the process, and in the latter case it is set free from the ammonium sulphate. The author criticises some earlier work dealing with the utilisation of various nitrogenous substances by plants, especially that of Czapek, Brenner, and Puriewitsch. He shows that certain factors have been left out of account in drawing conclusions from experimental results. More especially, he shows

that the acidity of the medium is to be taken into account, which may be due to the acid derived from the salts. His own experiments on the formation of soluble starch require the presence of acid. Furthermore, in estimating the yield of the moulds, no account has been taken of proteoclastic action, in that a mould may grow, and after a time the amount will diminish owing to this action. This factor again is influenced by the presence of acids.

S. B. S.

**Basis of Measurement of Antagonism.** W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **34**, 363—368).—A theoretical paper in which the possible methods of measuring the antagonistic action of salts on the growth of plants and animals is discussed.

H. W. B.

**The Relation of some of the Rarer Elements in Soils and Plants.** W. O. ROBINSON, L. A. STEINKOENIG, and C. F. MILLER (*U.S. Dept. Agr., Bull.*, 1917, No. 600; from *Physiol. Abstr.*, 1918, **3**, 75).—About fifty samples of legumes, grasses, vegetables, trees, and shrubs grown on nine soils of known composition, or obtained from localities where certain rare elements were known to occur, were examined. Lithium was found in spectroscopic traces in all the plants examined (max. 0.00015%). Rubidium was found in most cases and in larger quantities than the other rare alkalis (max. 0.025%), and in the cases where the amount of rubidium oxide exceeded 0.01% in the plant, minerals containing this element were known to occur in the soil. Cesium was found in only three plants obtained from a locality where cesium beryls occur. Chromium was occasionally found, although always in small quantities. Vanadium was only detected in six cases, and then in traces. Molybdenum was not found. Barium was found in all samples and strontium in all but one, and titanium occurred in minute quantities in all samples. With two exceptions, all the plants contained aluminium, the percentage in pine needles being exceptionally high (max. 0.253%). Methods of analysis are given in an appendix.

W. G.

**Flavone Derivatives in Plants. III. Tropical Plants.** K. SHIBATA and I. NAGAI (*Bot. Mag., Tokyo*, 1916, **30**, 149—178; from *Physiol. Abstr.*, 1918, **3**, 68—69).—The leaves, sprouts, blossoms, bark, and wood of two hundred and forty-two species were examined, and it was found that flavones were invariably present. The flavone glucosides of the cell sap exert a protective action against the solar rays, especially those of short wave-length. Thus plants grown under glass for some time contained less flavone than those grown in the open, and those grown in the shade less than those grown in the sun. Plants provided with a heavy cuticular layer were usually poor in flavones. The function of the flavone in the cell sap of the plants is similar to that of the pigment of the human skin. Flavone and anthocyanin often inter-

change. Thus young sprouts frequently contain anthocyanin-red, which changes into the colourless flavone glucoside in the grown organ, and back again into anthocyanin before the fall of the leaves. The winter buds of many plants contain flavones both in the tissues of the lower leaves and the viscous exudate. In many cases, the wax-like or powdery covering of the plant organs contains flavone compounds secreted by the epidermis [compare Müller, T., 1915, 107, 872]. W. G.

**Some Constituents of the American Grapefruit (*Citrus decumana*).** HARPER F. ZOLLER (*J. Ind. Eng. Chem.*, 1918, 10, 364—374).—Analyses of grapefruit showed that the peel contained 2.5 to 6.0 grams per fruit of essential oils, principally *d*-limonene (90—92%), with small quantities of citral,  $\alpha$ -pinene, geraniol, and linalool; also about 0.2 to 1.6 grams of the glucoside naringin per fruit and about 4 grams of pectin. The pulp contains about 1.9 to 6.0 grams of citric acid, 6.2 to 15 grams of sucrose, and 8.6 to 19.6 grams of dextrose per fruit. [See, further, *J. Soc. Chem. Ind.*, 1918, 387A.] W. F. F.

**A New Compound in Hyssop Killed by Fungus.** O. TUNMANN (*Pharm. Post*, 1917, 50, 773—774; from *Chem. Zentr.*, 1918, i, 29—30).—The cells of some hyssop plants which had been killed by moulds were found to contain as the chief crystalline deposit a colourless substance which has m. p. 275°, yields protocatechuic acid on fusion with potassium hydroxide, and is probably a flavone derivative. It is designated *hyssopin*, and resembles, but is not identical with, hesperidin, which has already been found in unusually large quantity in mint killed by fungus. J. C. W.

**Non-protein Nitrogen of Wheat Flour.** M. J. BLISH (*J. Biol. Chem.*, 1918, 33, 551—559).—The proteins are precipitated from an aqueous extract of wheat flour by treatment first with *N*/10-sodium hydroxide and then with *N*/10-copper sulphate solution, the non-protein nitrogen being subsequently estimated in the filtrate. Wheat flour contains 2 mg. of amino-acid nitrogen and 6 mg. of amide nitrogen per 100 grams of flour, as well as a considerable amount of non-protein nitrogen in an unknown form. [See also *J. Soc. Chem. Ind.*, 1918, 279A.] H. W. B.

**Boron. Its Effects on Crops and its Distribution in Plants and Soils in Various Parts of the United States.** F. C. COOK and J. B. WILSON (*Proc. Amer. Soc. Biol. Chem.*, 1917, vi—vii; *J. Biol. Chem.*, 1918, 33).—Boron in the form of borax or colemanite (calcium borate) is an effective larvicide for the housefly; care must be exercised in the subsequent distribution of manure to which it has been added, because small percentages of boron in some soils are found to exert a toxic action on certain plants, especially the *Leguminosae*. [See also *J. Soc. Chem. Ind.*, 1918, 274A.] H. W. B.

## General and Physical Chemistry.

### Double Refraction and Optical Activity of Liquid-Crystalline Substances.

FELIX STUMPF (*Jahr. Radioakt. Elek. tronik*, 1918, 15, 1—64).—A useful and detailed résumé, including bibliography, of the work since the earlier résumé in the same journal by R. Schenck in 1909, is given in six chapters, entitled: (1) Double refraction of inactive and active substances. (2) Rotation of plane of polarisation. (3) Theory of uniaxial active absorbing crystals. (4) Observations on the state of polarisation oblique to the axis of the advancing waves. (5) The theory of M. Born and its experimental examination. (6) The action of the magnetic field on liquid-crystalline substances. F. S.

### Anomalous Molecular Distribution in Mixed Crystals as the Cause of their Anomalous Double Refraction.

G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 226—235; from *Chem. Zentr.*, 1918, i, 567).—A consideration as to the cause of the internal strains to which the anomalous optical properties of some mixed crystals have been attributed. It is not very probable that during rapid crystallisation correct distribution of the components can occur completely so that the blending is entirely consistent with the symmetry of the space lattice. The disturbance in the molecular distribution will cause a reduction in the linearity of crystallisation and a deviation in the properties of the mixed crystal from those expected from its symmetry; both these effects are frequently observed. If an anomalous mixed crystal represents an unstable system, the solubility should be least for the normal mixed crystal, as has, indeed, been observed. It is calculated that the alteration in solubility to be expected from the effect of the internal strains in a certain case is 0.3%, whereas the observed difference in solubility may attain 50%. According to this result, the abnormal arrangement in the crystal lattice exerts a direct influence, and not merely an indirect effect on account of the internal strains. D. F. T.

### Electrical Double Refraction in Liquids.

C. BERGHOLM (*Ann. Physik*, 1917, [iv], 54, 511—518).—The author discusses the question of the dependence of the electrical double refraction on the composition and constitution of organic compounds, and points out that Kerr's constant cannot be considered to offer a suitable basis for the comparison of different substances. In place of Kerr's constant  $B$ , the quantity  $B_K = B\lambda nM / (K + 2)^2(n^2 + 2)^2d$  is proposed,  $\lambda$  being the wave-length of the light used,  $n$  the ordinary refractive index,  $M$  the molecular weight of the substance,  $K$  the dielectric constant, and  $d$  its density. The quantity  $54B_K$  represents the "electrical double refraction of the molecular refraction"

for a layer of liquid 1 cm. in thickness and an electrostatic field of unit intensity. The values of  $B_R$  for a number of substances are compared, and from this it would seem that in the case of aromatic compounds which have similar absorption spectra, the value of  $B_R$  varies but little with the nature of the substituent element or group and its position in the benzene ring.

H. M. D.

**The Light Emission of Gases and Mixtures of Gases by Electric Discharges.** L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 1043—1048).—A summary is given of experiments in which the effect of pressure and of the intensity of the electric discharge on the emission spectra of certain gases and gas mixtures was examined.

The observations made with nitrogen, hydrogen, neon, and helium show that the intensity of the lines and bands is proportional to the energy of the discharge, and that the maximum emission is displaced towards the ultra-violet when the pressure is decreased. Argon behaves quite differently, and the nature of the divergence depends on whether the red or the blue spectrum is emitted. If the intensity is plotted against the strength of the current, curves are obtained which are concave or convex to the current axis, according to whether the red or the blue spectrum is considered.

Observations made on mixtures of non-reactive gases show that there is generally a shift of the maximum towards the ultra-violet which may be interpreted in terms of the pressure effect referred to above. In the case of mixtures of gases which react with each other, the observations show that new bands make their appearance in the discharge spectrum.

H. M. D.

**Absorption of Ultra-violet Rays by Phenyl Derivatives of Methane.** G. MASSOL and A. FAUCON (*Compt. rend.*, 1918, 166, 819—821).—A study of the absorption spectra of benzene, toluene, and di- and tri-phenylmethanes. The results indicate that benzene and the three phenyl derivatives of methane show a general transparency for the radiations extending from the visible spectrum to  $\lambda=270$  and a selective absorption for the radiations from  $\lambda=270$  to  $\lambda=230$ . This selective absorption varies with the different compounds, and the characteristic spectrum of benzene with its narrow bands and its undulating aspect is not found in the phenyl derivatives of methane. Their bands are less numerous, often slightly displaced, and do not all appear at the same time. The transparency diminishes as the molecular weight increases. W. G.

**Confirmation of van't Hoff's Hypothesis. Optical Superposition in the Meta-saccharins and Related Substances.** EDWIN A. HILL (*J. Amer. Chem. Soc.*, 1918, 40, 764—773).—The question of the validity of the principle of optical superposition has been examined by reference to the rotator powers of the four meta-saccharins and of their strychnine, brucin

and quinine salts. It is shown that the specific and molecular rotations may be satisfactorily represented as the algebraic sums of three constants corresponding with the active  $\alpha$ -,  $\gamma$ -, and  $\delta$ -carbon atoms. The calculated constants for the  $\alpha$ - and  $\gamma$ -carbon atoms are very nearly the same for all the salts, but differ considerably from the  $\alpha$ - and  $\gamma$ -constants for the saccharins themselves. This is quite in accordance with the fact that ring structure is present in the saccharins, whilst the salts are characterised by chain structure. The sum of the activities of the  $\delta$ -carbon atom and the active base remains constant for the four salts corresponding with each of the three bases, but changes its value with the nature of the alkaloid.

By using the average values of the constants and calculating the specific rotations of the twelve salts, it is found that the average differences between the calculated and observed rotations are  $0.94^\circ$  for the strychnine salts,  $0.25^\circ$  for the brucine salts, and  $0.22^\circ$  for the quinine salts.

Reference is made to other recorded data which afford evidence of the validity of the principle of optical superposition.

H. M. D.

**Action of Light-rays on Organic Compounds and the Photosynthesis of Organic from Inorganic Compounds in Presence of Inorganic Colloids.** BENJAMIN MOORE and T. A. WEBSTER (*Proc. Roy. Soc.*, 1918, [B.] **90**, 168—186).—In the formation of formaldehyde from carbon dioxide in light in the presence of an inorganic catalyst, it is shown that the action depends, not only on the specific character of the catalyst, but also on its state of aggregation. Exposure of formaldehyde solutions to light lead to the formation of condensation products which reduce Benedict's solution. The relationship between the osmotic energy and thermochemical relations in reversible reactions of this description is discussed. The authors also discuss generally the formation of formaldehyde by phytochemical decomposition of more complex substances.

S. B. S.

**The Parent of Actinium.** FREDERICK SODDY and JOHN A. CRANSTON [and, in part, ADA HITCHINS] (*Proc. Roy. Soc.*, 1918, [A.] **94**, 384—404).—The history of the long search for the parent of actinium, and of the various theories that have been framed to connect it with uranium, is dealt with in full. The present work was undertaken to test the hypothesis that actinium is produced from "eka-tantalum," the missing element between uranium and thorium in the Periodic Table, by its disintegration in a slow  $\alpha$ -ray change, giving actinium. Eka-tantalum is probably the product of uranium-Y, discovered by Antonov (A., 1911, ii, 844; 1914, ii, 17), and it should be isotopic with uranium-X<sub>2</sub> or brevium.

It was found that uranium-X<sub>2</sub> could be effectively separated from uranium-X<sub>1</sub>, isotopic with thorium, by distillation at a dull red heat in chlorine charged with carbon tetrachloride vapour, the uranium-X<sub>2</sub> volatilising. The attempt was made to separate eka-



tantalum from pitchblende similarly. About 500 grams of a very pure Indian pitchblende ( $\text{U}_3\text{O}_8$  86%,  $\text{PbO}$  11.9%,  $\text{ThO}_2$  1.9%,  $\text{SiO}_2$  0.6%) similarly treated gave three sublimates, the first after twenty-two hours, the second after ninety hours further, and the last [prepared by (Miss) A. Hitchins] after six hours at a much higher temperature. These sublimates were kept under observation for the growth of actinium, from which they were initially free. The presence of actinium was tested for by means of its characteristic active deposit. The second sublimate, in the course of one thousand days, produced a quantity of actinium twenty times greater than could be with certainty detected. So far as can yet be seen, the rate of growth of actinium appears to be linear with the time, pointing to a direct production. The other preparations have remained free from actinium. Another preparation, from Joachimsthal pitchblende, treated similarly, gave a sublimate also giving actinium with time. For the second sublimate from Indian pitchblende, the attempt was made to compare the quantity of actinium present after 2.5 years with that in the originating pitchblende. The amount of actinium present was found to be the same as that in 0.25 gram of the pitchblende. On the assumptions (1) that the actinium is produced in a direct change, (2) that the sublimate contained all the parent of actinium present in the original mineral, the period of average life of actinium is calculated to be 5,000 years. The quantitative measurement by radio-active methods of minute quantities of actinium by means of its emanation and active deposit presents difficulties which have not been completely overcome. The work supports the theory of the origin of actinium, referred to at the beginning, but does not finally establish it to the exclusion of all other possible modes of origin.

F. S.

### Mobilities of Ions in Air, Hydrogen, and Nitrogen.

KIA-LOK YEN (*Proc. Nat. Acad. Sci.*, 1918, 4, 91—97).—The mobilities of the positive and negative ions in air, hydrogen, and nitrogen have been measured at various pressures and for widely different potentials. The results show that the mobility varies inversely as the pressure, and that the product of these quantities is independent of the strength of the field in the case of both positive and negative ions. The results are discussed with reference to the constitution of the ions, and the author contends that they afford support for the view that the ions consist of a single atom or molecule, as opposed to the cluster hypothesis according to which an ion is supposed to consist of a relatively large group of satellite molecules. The fact that the mobility of the negative ions is in all cases greater than that of the positive ions can be readily explained in terms of the simple ion hypothesis when the relative magnitude of the forces acting between neutral molecules and ions of opposite sign is taken into account. This attractive force is greater for the positive ion, and, in consequence, the effective mean free path of the positive ion is less than that of the negative ion.

The reduced mean free path involves a diminution in the mobility of the positive ions as compared with that of the negative ions.

H. M. D.

**Mobilities of Ions in Vapours.** КИЯТЛОК YEN (*Proc. Nat. Acad. Sci.*, 1918, 4, 106—109).—The mobilities of the positive and negative ions in sulphur dioxide, acetaldehyde, ethyl chloride, ethyl alcohol, pentane, acetone, ethyl acetate, ethyl iodide, and methyl iodide have been measured at various pressures. The mean values obtained show that the mobility of the negative ion is slightly greater than that of the positive, except in the case of ethyl iodide, for which the observed values are the same. The ratio of the mobilities of the oppositely charged ions in these vapours is much smaller than the ratio found in the case of air, hydrogen, and nitrogen, and is quite in accordance with the assumption that the ions are simple in type (compare preceding abstract). H. M. D.

**The Distribution of Radioactive Gases in the Free Atmosphere.** VICTOR F. HESS and WILHELM SCHMIDT (*Physikal. Zeitsch.*, 1918, 19, 109—113).—From the point of view of present knowledge of the interchange going on in the free air by virtue of the random molecular motion, the law for the distribution with height of a radioactive gas in the atmosphere and the comparison of the amount at any altitude with that present at the earth's surface have been worked out. The calculated values agree with such observations as have been made for the radium emanation, so far as the order of magnitude is concerned. The calculated values, for the height in which the quantity of the radioactive material per gram of air is reduced to half the value at the surface, are:

Radium emanation and its short-lived products, about 1200 metres.

Radium-*D* and subsequent products, uniform up to 10 kilometres.

Thorium emanation and thorium-*A*, 2 to 3 metres.

Thorium-*B* and subsequent products, 100 to 150 metres.

Actinium emanation and actinium-*A*, 0.5 to 1 metre.

Actinium-*B* and subsequent products, 10 to 20 metres.

The total quantity of radium emanation in the whole atmosphere is estimated as between 1.6 and  $2.3 \times 10^7$  Curies.

F. S.

**Attempted Separation of Isotopic Elements by means of Fractional Diffusion.** H. LACHS, M. NADRATOWSKA, and L. WERTENSTEIN (*Compt. rend., Soc. Sci. Warsaw*, 1917, 9, 370—372; from *Chem. Zentr.*, 1918, i, 416).—In an attempt to separate the isotopes  $U_1$  and  $U_2$  by the fractional diffusion of a solution of uranyl nitrate, no difference was observable between the radioactivity of the diffusate and of the original substance. If there is any difference between the diffusion coefficients of the two isotopes, it cannot be greater than 1.5%.

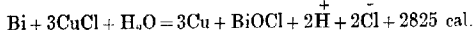
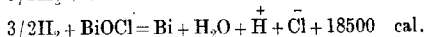
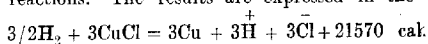
D. F. T.

**Can the Production of Electricity by Organic Substances and Living Tissue be Explained by known Thermodynamic Laws?** R. BEUTNER (*Zeitsch. Elektrochem.*, 1918, **24**, 94—100).—Polemical against Baur and Kronmann (*A.*, 1917, ii, 231). It is shown that the production of the current in two-phase liquid elements can be explained thermodynamically, and, consequently, the production of the biological current can also be explained in the same way. It is claimed that the absorption theory of Baur, which is put forward to take the place of the thermodynamic theory, is therefore superfluous, and, furthermore, unproved. J. F. S.

**Can the Production of Electricity by Organic Substances and Living Tissues be Explained by known Thermodynamic Laws?** EMIL BAUR (*Zeitsch. Elektrochem.*, 1918, **24**, 100—101).—Polemical, an answer to Beutner (see preceding abstract). J. F. S.

**Potentials of the Bismuth-Bismuth Oxychloride and the Copper-Cuprous Chloride Electrodes.** ARTHUR A. NOTES and MING CHOW (*J. Amer. Chem. Soc.*, 1918, **40**, 739—763).—The normal potentials have been derived from measurements of the *E.M.F.* of cells formed by combination of the bismuth oxychloride and cuprous chloride electrodes with the hydrogen electrode and with each other. The mean values obtained for the normal potential of the bismuth oxychloride electrode are  $-0.1635$ ,  $-0.1599$ , and  $-0.1563$  volt at  $15^\circ$ ,  $25^\circ$ , and  $35^\circ$  respectively. The corresponding values for the cuprous chloride electrode are  $-0.1263$ ,  $-0.1200$ , and  $-0.1132$  volt respectively.

From the temperature coefficients of the electrode potentials, the authors have calculated the heat changes accompanying the chemical reactions. The results are expressed in the equations



By measuring directly the heat of the reaction between metallic tin and bismuth oxychloride, and also of the reaction between tin and cuprous chloride in presence of dilute hydrochloric acid, the value found for the last of the above reactions is 7390 cal., which is very much larger than that indicated by the potential measurements. The discrepancy has not yet been accounted for.

The equilibrium corresponding with the equation  $\text{Bi} + 3\text{CuCl} + \text{H}_2\text{O} \rightleftharpoons 3\text{Cu} + \text{BiOCl} + 2\text{H} + 2\bar{\text{Cl}}$  has been determined by experiments at  $75^\circ$ . The constant  $K_{75} = [\text{H}]^2 \cdot [\bar{\text{Cl}}]^2$  has the value  $2.10 \times 10^{-3}$ . H. M. D.

**Electrical Endosmose. II.** T. R. BRIGGS, H. S. BENNETT, and H. L. PIERSON (*J. Physical Chem.*, 1918, **22**, 256—272. Compare *A.*, 1917, ii, 236).—An improved form of electro-osmometer

is described which consists essentially of a horizontal tube containing the diaphragm, in close proximity to which are the electrodes, which pass through vertical side tubes which permit of the escape of gases generated during the passage of the current. The anode and cathode compartments are also connected through a narrow tube which contains an air bubble. This tube is provided with a scale, and the rate at which the bubble moves along the tube affords a measure of the electro-endosmotic flow.

Measurements have been made which show the dependence of the effect on the applied potential difference, the temperature, and on the nature of the diaphragm and of the dissolved electrolyte.

The rate of endosmotic flow is proportional to the applied difference of potential. For a given potential, it increases with rise of temperature, the rate of increase being somewhat smaller than that of the fluidity.

The results obtained in the investigation of dilute acid and alkaline solutions confirm the observation, made by Perrin, that the direction of flow undergoes reversal on passing from an acid to an alkaline solution. With a carborundum diaphragm, the isoelectric point was found to correspond with a very slightly acid solution. Sharp reversals were also obtained with alundum and also with diaphragms of gelatin and agar jellies. With powdered glass, no reversal was obtained.

Observations made with various copper salts are also recorded, and the bearing of the electro-endosmotic effects on the electrical and adsorption theories of dyeing is discussed in reference to some experiments made with acid and basic dyes. H. M. D.

**The Abnormality of Strong Electrolytes. I. Electrical Conductivity of Aqueous Solutions.** JNANENDRA CHANDRA GHOSH (T., 1918, 113, 449—458).—The fact that the ionisation of strong electrolytes, as measured by the electrical conductivity or osmotic methods, does not vary with the dilution in accordance with the requirements of the law of mass action, is supposed to be due to the invalidity of the fundamental idea underlying the Arrhenius ionic theory. According to the author, strong electrolytes are completely ionised, and there is no question of an equilibrium between ions and unionised molecules. The relations between the ions are determined solely by the electrical forces acting between the ions, and the interior of a solution of a strong electrolyte is characterised by a certain potential,  $A$ , which affords a measure of the work which is required to remove the ions from the influence of their mutual attractive forces. By application of the kinetic theory, it may be inferred that ions become "free" when their velocity exceeds a certain critical value. The fraction of the free ions is equal to  $e^{-A/nRT}$ , in which  $n$  is the number of ions formed from a molecule of the electrolyte. Denoting the Avogadro number by  $N$ , then the number of free ions is  $nNe^{-A/nRT}$ . At infinite dilution  $A=0$ , and the number of free ions  $=nN$ . From this follows  $A = nRT \log_e \mu_\infty / \mu_v$  (1).

Assuming that the marshalling of the ions in solution corre-

sponds with the arrangement of the atoms in the crystallised electrolyte, and that the component ions form a completely saturated electrical doublet, it is possible to calculate  $A$  from the charge  $E$  carried by the ions and  $r$  their distance apart. In the case of a binary electrolyte, the equation is  $A = E^2 / Dr$ , where  $D$  is the dielectric constant of the solvent medium and  $r = \frac{2}{3} v / 2N$  (2). From equations (1) and (2), the value of  $\mu_e$  may be calculated for varying dilutions, and it is shown that the calculated values are in close agreement with those found by experiment between  $v=10$  and  $v=5000$ . The agreement is also good in the case of ternary electrolytes. For bi-bivalent electrolytes, agreement is found for dilutions between  $v=10$  and  $v=100$ , but at  $v=1000$  the observed conductivities are much greater than those calculated from the author's formula. The discrepancy is said to be due to hydrolysis.

On account of the diminution of the dielectric constant with rise of temperature, the value of  $\mu_e / \mu_\infty$  should decrease. The observed diminution for potassium chloride at  $100^\circ$  is shown to be in satisfactory agreement with that calculated from the author's formula.  
H. M. D.

**"The Magnetic Properties of Zinc Blende and some other Minerals."** F. STUTZER, W. GROSS and K. BORNEMANN (*Metall und Erz*, 1918, 15, i, 1—9).—A method is described for measuring the magnetic susceptibility of paramagnetic minerals such as zinc blende, and a list of values of this constant given for fifty-three samples.  
F. C. T.

**Theoretical and Experimental Investigation of the Thermal Conductivity of Mixtures of Gases.** SOFUS WEBER (*Ann. Physik*, 1917, [iv], 54, 481—502).—The theory of the thermal conductivity of gas mixtures is discussed in reference to the experimental data recorded in the literature. New measurements have been made for mixtures of hydrogen and carbon dioxide and of nitrogen and argon, and it is found that the results may be satisfactorily represented by the formula

$$K = K_1 / (1 + A p_2 / p_1) + K_2 / (1 + B p_1 / p_2),$$

in which  $K_1$  and  $K_2$  are the thermal conductivities of the constituent gases,  $p_1$  and  $p_2$  the partial pressures of the components in the mixture for which the conductivity is  $K$ , and  $A$  and  $B$  are empirical constants. These constants differ very widely from those which are indicated by theory. In the case of mixtures of hydrogen and carbon dioxide, the values of the constants indicated by theory are  $A=1.01$  and  $B=2.56$ , whilst the empirical values which satisfy the experimental results are  $A=2.70$  and  $B=0.40$ . For mixtures of nitrogen and argon, the empirical values are  $A=1.07$  and  $B=0.95$ . Since the constants are in this case nearly equal, it follows that the thermal conductivity of mixtures is approximately given by the mixture formula, according to which  
 $K = K_1 \cdot p_1 / (p_1 + p_2) + K_2 \cdot p_2 / (p_1 + p_2)$ .  
H. M. D.

**Theory of Specific Heats.** CARL DRUCKER (*Zeitsch. Elektrochem.*, 1918, 24, 83—84).—Polemical, in which the author

criticises the method employed by Jankowsky (this vol., ii, 59) in deducing certain relationships for the specific heat of gases. The deductions drawn from the mathematical expressions are also criticised.

J. F. S.

**Specific Heat at Low Temperatures. IV. Measurements of the Specific Heat of Liquid Hydrogen. Preliminary results on the Specific Heat of Solid Hydrogen and on the Heat of Fusion of Hydrogen.** W. H. KEESOM and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 1000—1004. Compare A., 1916, ii, 371).—The apparatus previously described has been used in the determination of the specific heat of liquid hydrogen. According to the most complete of several series of measurements, the atomic heat increases from 1.75 at 14.82° (abs.) to 2.26 at 20.11°.

The data obtained for solid hydrogen gave a mean value of 0.64 at 12.55° for the atomic heat, and for the latent heat of fusion the value 15 was obtained as the mean of two experiments.

H. M. D.

**Specific Heats of Lead-Antimony Alloys.** R. DURRER (*Physikal. Zeitsch.*, 1918, 19, 86—88).—Within the limits of experimental error, the specific heat of alloys of lead and antimony agrees with that calculated from the specific heats of the components by the simple mixture rule. The specific heat (between 0° and 300°) is actually represented by the equation

$$S = 0.04965 - 0.0001884 p,$$

where  $p$  is the percentage of lead in the alloy. The freezing-point diagram for this pair of metals shows that there are two curves meeting in a eutectic point at 249°.

H. M. D.

**Atomic Heats of Tungsten and Carbon at Incandescent Temperatures.** A. G. WORTHING (*J. Franklin Inst.*, 1918, 185, 707—708).—Many of the theories, based on the quantum hypothesis, for explaining the variation of the atomic heat with temperature, lead to the value 5.95 cal. per gram-atom degree as the upper limit for this quantity. With the object of testing these conclusions, the atomic heats of tungsten and carbon have been determined at high temperatures. The elements were used as filaments contained in closed globes at constant pressure; the heating was electrical, and the rate of cooling was determined by means of a potentiometer and a pendulum which operated switches at various points in its path. In the case of tungsten, the atomic heat is shown to vary almost linearly from 6.25 cal. per gram-atom degree at 1200° to 7.35 cal. per gram-atom degree at 2400°. That is, at these temperatures it has an atomic heat which is considerably above the theoretical maximum value, 5.95. In the case of carbon, the value varies from 5.35 at 1200° to 6.05 at 2000°.

J. F. S.

**Melting Point Apparatus.** J. C. HIBBERT and W. F. THOMPSON (*Analyst*, 1918, 43, 216).—A test-tube, 7 inches by 1.4

inches, is supported in a clamp and closed by a cork; the thermometer is attached to a glass tube passing through the cork. The stirrer also passes through a slot in the cork and is supported by rubber rings connected with a bent wire fixed to the clamp stand. The burner is provided with a glass wind-screen. W. P. S.

**Sulphur as a Cryoscopic Solvent.** E. BECKMANN and C. PLATZMANN (*Zeitsch. anorg. Chem.*, 1918, **102**, 201—214).—In spite of the facility with which it undergoes transformation into allotropic modifications, sulphur can be successfully used as a cryoscopic solvent if certain conditions are fulfilled. Soon after having been melted, the freezing point of sulphur is about  $119^{\circ}$ , but after it has been kept for some hours at a temperature just above its melting point, the freezing point falls to  $114.5^{\circ}$ , and in this condition the sulphur is suitable for cryoscopic determinations. The apparatus and method employed have been previously described (A., 1897, ii, 88).

The cryoscopic constant of sulphur was determined by means of a number of organic compounds, bromoform (229.3), phenylthiocarbimide (226.6), naphthalene (211.4), diphenyl (208.4), thymol (206.4), quinoline (205.7),  $\beta$ -naphthol (205.2), and aniline (201.8), the mean value of  $K$  being 213. The latent heat of fusion  $w$ , calculated from van't Hoff's equation, is 14.1 gram cal., a value somewhat higher than that determined experimentally for monoclinic sulphur. In accordance with its low dielectric coefficient, 4.0, sulphur shows no dissociating power. Substances of an acidic character like *p*-cresol and  $\alpha$ -naphthoic acid show a tendency to associate to double molecules, the value of  $K$  falling with increasing concentration.

The "natural" m. p. of sulphur,  $114.5^{\circ}$ , corresponds with a content of about 3.6%  $S_8$ . The observation of A. Smith (A., 1907, ii, 20), that the attainment of a steady m. p. by sulphur is delayed by sulphur dioxide and accelerated by ammonia, is confirmed. Organic compounds of a neutral or acidic character resemble the former, whilst basic substances, such as pyridine and aniline, resemble ammonia in their behaviour. These substances act catalytically by delaying or accelerating the formation of  $S_8$ , which may itself, however, be formed from  $S_2$ .

Arsenic trisulphide in sulphur has the simple molecule  $As_2S_3$ , but tends to polymerise with increasing concentration. Selenium tetrachloride shows a molecular weight of half the normal value, and this is attributed to the formation of selenium and sulphur monochlorides. E. H. R.

**Measurement of Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature.** P. G. CATH and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 991—999. Compare A., 1914, ii, 27).—An improved form of helium gas thermometer is described, and an account is given of the apparatus and

methods employed in the further measurement of the vapour pressure of liquid hydrogen at temperatures ranging from the boiling point to the critical point.

H. M. D.

**The Saturated Vapour Pressures of Tetratomic Substances.** E. ARIÈS (*Compt. rend.*, 1918, 166, 802—805).—On the basis of the vapour pressures of ammonia given in the *Recueil de Constantes physiques*, the formula for the saturated vapour pressures of tetratomic substances is given as  $\Pi = r^{12.6} Z/x$ , where  $x = [1 + (1 - r)(0.84 - r)/(\tau^2 + 1)]\tau^{11.6}$ . Whilst the observed values for phosphorus trichloride are in fair agreement with those calculated from this formula, the agreement is not so good in the case of acetylene.

W. G.

**The Association of Organic Compounds in Benzene and Alcohol Solution as determined by the Vapour Pressure Method.** WILLIAM ROSS INNES (T., 1918, 113, 410—435).—The vapour pressures of benzene and ethyl alcohol when mixed with varying quantities of non-volatile substances have been measured at certain fixed temperatures. From the experimental data, the author has calculated the apparent molecular weight of the non-volatile substance by making use of the equation for Raoult's law. If  $g$  grams of the substance of molecular weight  $m$  are dissolved in  $G$  grams of the volatile solvent of molecular weight  $M$ , and the vapour pressures of the pure solvent and solution are  $p$  and  $p'$ , then this equation may be written in the form  $m' = gMp'/G(p - p')$ , where  $m'$  is the apparent molecular weight of the non-volatile solute. The results obtained are shown by means of curves, in which  $m'/m$  is plotted as a function of the percentage molecular concentration of the solute.

When benzene is used as solvent, the curves obtained may be divided into groups. In one of these, the substances have values of  $m'/m$  which differ but little from unity even when the molecular concentration of the substance is very large. Acids and oximes form a group showing considerable association. In the case of formanilide and acetanilide, the value of  $m'/m$  increases rapidly with the concentration, and a maximum appears to be reached. Ethyl tartrate is extremely abnormal in that very high values are found for  $m'/m$ , which reaches a maximum when the percentage molecular concentration is about 50 and diminishes rapidly at higher concentrations.

In alcohol as solvent, four substances were examined, and all gave values of  $m'/m$  which increase with the concentration. In the case of azobenzene, which is readily soluble in hot alcohol, the association factor seems to increase continuously with the concentration. The value of  $m'/m$  obtained for this substance in 60% solution is about 6.0.

The theoretical interpretation of the results is discussed in some detail, and in this connexion attention is directed to results obtained for mixtures of sulphuric acid and water (compare T.,



1904, 85, 1345), according to which the apparent molecular weight is very small and decreases rapidly with increasing concentration.

H. M. D.

#### Heats of Dilution and their Variations with Temperature.

FRANK R. PRATT (*J. Franklin Inst.*, 1918, 185, 663—695).—The heat of dilution of solutions of a large number of salts has been determined at a series of temperatures with the object of testing the validity of the expression  $dl/d\theta = -dH/dm$ , in which  $l$  is the heat of dilution,  $\theta$  the temperature,  $m$  the mass of the solution, and  $H$  the heat capacity of the system. The measurements were made by the method of constant flow, in which two streams, of solution and water respectively at the same temperature, were allowed to mix continuously in a Dewar vessel at constant temperature. Solutions of sodium chloride, potassium chloride, barium chloride, strontium chloride, ammonium chloride, sodium hydroxide, potassium hydroxide, sodium nitrate, potassium nitrate, barium nitrate, strontium nitrate, and ammonium nitrate were used. The results indicate that in a general way the above formula is true. The discrepancies are discussed. A further series of measurements was made with the following non-electrolytes: resorcinol, dextrose, sucrose, catechol, quinol, mannose, and ethyl alcohol. The chief point of interest arising from these experiments is that for non-electrolytes  $H$  is constant for all concentrations; on the whole the results here are in general agreement with the above formula.

J. F. S.

#### Possibility of Calculating the Properties of Liquids and Vapours.

JOHANNES GEISSLER (*Zeitsch. Elektrochem.*, 1918, 24, 101—113).—A theoretical paper in which the author has shown that for the four substances fluorobenzene, benzene, ethyl ether, and carbon tetrachloride there is a region in which the physical properties can be represented by straight lines, and that within the limits of this area the physical properties can be calculated. Methods are worked out for calculating (1) the molecular volume of the saturated vapour from that of the liquid, (2) the molecular volume of a liquid from the temperature, (3) the coefficient of expansion of a liquid from the temperature, (4) the vapour pressure of a liquid from the temperature, (5) the change of vapour pressure per degree at a given temperature, (6) the latent heat of vaporisation of a liquid at a given temperature. The calculated and experimental values are compared, and it is shown that whilst there is good agreement in many cases, there are also divergences. The latter are attributed to the use of data obtained in a region removed from the limited region mentioned above, or from data in the neighbourhood of the freezing point.

J. F. S.

#### Atomic and Molecular Numbers.

HERBERT STANLEY ALLEN (*T.*, 1918, 113, 389—396).—A short account is given of the significance of the atomic number in connexion with the periodic

classification of the elements. The atomic numbers of analogous elements differ by eight or a multiple of eight, or in some cases by a number which is two units greater than one of the foregoing. The reason for these variations from the rule of eight is the presence of three elements in group VIII of the periodic table.

Molecular numbers of analogous compounds show similar relations. In reference to organic compounds, it is pointed out that the molecular number for the group  $\cdot\text{CH}_2\cdot$  is eight, and the rule of eight is consequently of wide application in organic chemistry. It is probable that many properties of chemical compounds will be found to depend on the values of the molecular numbers.

H. M. D.

**Modified Mercurial Viscosimeter for Determining the Viscosity of Volatile Liquids.** F. M. LIDSTONE (*J. Soc. Chem. Ind.*, 1918, **37**, 148—149r).—In the apparatus described, an attachment is provided by means of which an equal excess pressure may be applied above and below the moving column of liquid in the viscometer. This prevents the formation of a cushion of vapour between the mercury and the volatile liquid under examination, but does not interfere with the usual constants of the instrument.

W. P. S.

**The Viscosity of Liquefied Gases. X. The Viscosity of Liquid Hydrogen.** J. E. VERSCHAFFELT (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 986—990. Compare A., 1917, ii, 408).—From observations on the time of oscillation of a specially designed oscillatory system immersed in the liquid hydrogen, the viscosity at  $20.4^\circ$  (abs.) has been found to be  $\eta = 0.000130$ , with an estimated accuracy of about 1%. A preliminary determination of the viscosity of the saturated vapour at this temperature (vapour pressure = 76.9 cm.) gave  $\eta = 0.000010$ .

H. M. D.

**Solubility Measurements.** STEWART J. LLOYD (*J. Physical Chem.*, 1918, **22**, 300—302).—The measurements recorded were made incidentally in connexion with other work. The solubility of sulphur dioxide in benzene, toluene, nitrobenzene, *o*-nitrotoluene, and acetic anhydride was measured at various temperatures. At  $20^\circ$ , the solutions saturated at 756—760 mm. contain the following amounts in grams per litre: toluene, 236.0; nitrobenzene, 267.4; *o*-nitrotoluene, 236.0; acetic anhydride, 106. The solubility of aluminium chloride in carbon tetrachloride decreases from 0.74 at  $1^\circ$  to 0.06 gram per litre at  $34^\circ$ ; in chloroform, from 1.00 at  $0^\circ$  to 0.72 at  $25^\circ$  and 0.65 at  $-15^\circ$ . The solubility of barium chloride in nitrobenzene increases from 0.167 at  $20^\circ$  to 0.40 at  $100^\circ$ , and that of benzoic acid in ethyl acetate from 8.0 grams per litre at  $-6.5^\circ$  to 37.7 at  $21.5^\circ$  and 95.7 at  $75^\circ$ .

H. M. D.

**Reactions between Solid Substances.** LESLIE HENRY PARRER (T., 1918, **113**, 396—409. Compare T., 1914, **105**, 1504).—The rate at which certain solid substances react together has

been examined systematically by observations at various temperatures up to and above the fusion temperature. The pairs of substances investigated were sodium carbonate and barium sulphate, silver nitrate and sodium carbonate, cuprous chloride and sodium carbonate. In all cases, the mixtures were made from carefully dried substances. Although the results obtained show clearly that reaction takes place below the fusion temperature, and that the rate of the reaction between the solids increases continuously with rise of temperature, there is in all cases a very marked increase in the velocity at the temperature of fusion. The ratio of the velocity in the fused mixture to that at the highest temperature in the solid state varies in the three cases examined. It is immeasurably large in the mixture containing barium sulphate, is equal to about 150 for the mixture containing silver nitrate, and to about 20 for the mixture containing cuprous chloride.

The results seem to show that the liquid state per se has an influence on the rate of interaction, which influence is to be distinguished from that of temperature. The fact that shearing stresses give rise to reactions between solid substances does not seem as yet to be completely explained, and it is suggested that such stresses produce changes of state in the surface layers which are equivalent to that produced by fusion.

H. M. D.

### **Xanthic Acids and the Kinetics of their Decomposition.**

I. HANS VON HALBAN and WALTER HECHT (*Zeitsch. Elektrochem.*, 1918, **24**, 65—82. Compare A., 1913, ii, 312).—The rate of decomposition of xanthic acid [ethyl hydrogen dithiocarbonate,  $\text{OEt-CS-SH}$ ] and methyl hydrogen dithiocarbonate in water at  $0^\circ$  has been studied. The solubility of these substances in water was first determined, and found to be at  $0^\circ$ : xanthic acid, 0.02 mol. per litre; methyl hydrogen dithiocarbonate, 0.05 mol. per litre. The rate of decomposition was determined by dissolving a known amount of the sodium salt of the acid in question in water, and, when the solution had reached  $0^\circ$ , liberating the acid with a slight excess of hydrochloric acid, then after a measured interval of time neutralising with a cooled solution of sodium hydrogen carbonate and titrating with a 0.02*N*-iodine solution. It is shown that, contrary to the behaviour of solutions in organic solvents, the velocity constants in the present case, when calculated on the basis of a unimolecular reaction, decrease rapidly with decreasing concentration; the decomposition is positively catalysed by hydrogen ions. This leads to the assumption that both the undissociated molecules and the ions take part in the reaction. On the basis of this assumption, the dissociation constants of the acids were calculated, and found to be independent of the dilution, a fact which confirms the assumption. At  $0^\circ$ , the dissociation constant for methyl hydrogen dithiocarbonate is found to be 0.034, and that for xanthic acid 0.030. The addition of sulphates (Na, Mg,  $\text{NH}_4$ ) to the decomposing xanthic acids in water solution strongly retards the action; for example, 0.25*N*-magnesium sulphate reduces the velocity of decomposition to one-third of the original value, and 3*N*-ammonium

sulphate reduces it to one-sixth. A few velocity measurements have been made in ethyl alcohol, methyl alcohol, propyl alcohol, amyl alcohol, and benzyl alcohol solutions to complete the data published in an earlier paper (*loc. cit.*). Measurements were made at 0° on the partition of xanthic acid between water and carbon disulphide, chloroform, nitrobenzene, light petroleum, benzyl alcohol, and amyl alcohol respectively. It is shown that the dependence of the partition coefficient on the dilution is in accord with the dissociation constant calculated from the velocity values. The absorption spectrum of solutions of xanthic acid in light petroleum, 0.5*N*-ethyl alcohol in light petroleum, and in diethyl ether was measured, but although the rate of decomposition is very different in the different solvents, no difference could be observed in the absorption curves. Benzyl hydrogen dithiocarbonate was prepared from the potassium salt. This substance is a solid, m. p. 29°, and when quite pure may be kept for several hours, and in non-hydroxy-solvents has a normal molecular weight. The solubility and rate of decomposition have been determined in twelve solvents. The saturated solution at 0° has the following concentration in these solvents: hexane 0.224*N*, light petroleum 0.316*N*, methyl alcohol 0.36*N*, acetic acid 0.41*N*, nitromethane 1.49*N*, acetonitrile 3.26*N*, carbon disulphide 3.70*N*, acetone 3.41*N*, diethyl ether 2.93*N*, benzene 3.33*N*, ethyl bromide 3.88*N*, and nitrobenzene 3.15*N*. The van't Hoff velocity constant was calculated from the data, and these values, as well as those for xanthic acid, show that the catalytic influence of the solvent is not removed by the van't Hoff calculation. J. F. S.

#### Hydrolysis of Ethyl Citrate and the Ethyl Hydrogen

**Citrates.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1918, **24**, 84–85).—Polemical; the author claims that the work of Pinnow (this vol., ii, 103) is not the first case in which the hydrolysis of a tribasic ester has been studied, and then proceeds to criticise the results published by Pinnow. J. F. S.

#### The Influence of Lipoids on the Rate of Reaction.

M. SIEGFRIED (*Biochem. Zeitsch.*, 1918, **86**, 98–109).—Lecithin inhibits the transformation of the yellow mercuric iodide into the red variety, and also the reduction of ammoniacal silver nitrate by phenylhydrazine. The latter reaction should be carried out in the dark, and in the presence even of diffuse sunlight the inhibiting action of the lipid is diminished. S. B. S.

#### Ester Catalysis of $\gamma$ -Lactones.

HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1918, **51**, 480–485).—It has recently been shown that the hydrolysis of  $\beta$ -lactones to the hydroxy-acids is not catalysed by hydrogen ions (*Lunds universitets årsskrift*, 1916), and it appeared to be of interest, therefore, to determine directly whether the hydrolysis of  $\gamma$ -lactones, like the formation of them (compare Taylor and Close, A., 1917, ii, 253), is catalysed by acids.

For this purpose, the catalysis of the hydrolysis of  $\gamma$ -valerolactone and  $\gamma$ -butyrolactone by nitric acid has been studied, the hydroxy-acid being titrated by means of barium hydroxide. It is found that in the case of  $\gamma$ -butyrolactone, with quantities of nitric acid represented by 9, 3, and 1, the time required for the production of the same percentage of hydroxy-acid is represented very nearly by 1, 3, and 9. The results with valerolactone are similar; H-ion concentration, 6:3:1 (roughly), and times, 1:3:6. The hydrolysis of  $\gamma$ -lactones is therefore a normal case of ester catalysis.

J. C. W.

**Errors affecting Determinations of Atomic Weight.**  
**VII. Refinements in the Method of Weighing: Microbalance: Application to the Atomic Weight of Helium and Hydrogen.** PH. A. GURE (*J. Chim. Phys.*, 1918, 16, 46—61. Compare A., 1916, ii, 385, 386, 432, 435; this vol., ii, 40, 41).—The Taylor microbalance is discussed by the author and shown to be very suitable for the accurate determination of gaseous densities. Correct formulæ are developed for calculation of the density and molecular weight of gases from the experimental figures obtained in this way. These formulæ have been applied to the experimental figures obtained by Taylor (*Phys. Review*, 1917, 10, 653), when the following values were obtained: normal litre of hydrogen weighs 0.089858 gram, molecular weight 2.0151; normal litre of helium weighs 0.17835 gram, molecular weight 3.9976. These values differ by about 10 per 10,000 from those calculated by Taylor. It is further shown that the Taylor microbalance appears to be susceptible of a few improvements, which are indicated by the author, and which, being made, give an instrument which will not only give the densities and molecular weights of gases with a precision at least equal to that of other methods, but which, with very small quantities of material, will give all the weighings necessary for the determination of atomic ratios. The great interest of the method lies in the fact that the determination of mass will resolve itself into the measurement of length, which is much more precise than weighing with weights, no matter how carefully calibrated.

J. F. S.

**The Conception of the Chemical Element and the Phenomenon of Isotopy (Addendum).** K. FAJANS (*Jahr. Radioaktiv. Elektronik*, 1918, 15, 101—102. Compare A., 1917, ii, 566).—In further pressing the point of view that isotopic elements cannot be considered as one element, in Boyle's sense of undecomposability, an intimate mechanical mixture of isotopes is postulated as capable of being made and of existing as such in nature, which, since they can be imagined to be capable of being resolved into their constituents, if of different density, by the use of suitable fluids, cannot be regarded as undecomposable.

F. S.

### Molecular Frequency and Molecular Number. III. Inorganic Compounds. Lindemann's Formula. H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], 35, 445—460. Compare this vol., ii, 163).

—According to Lindemann, the characteristic molecular frequency of a compound is given by the formula  $\nu = k\sqrt{T_s/MV^{\frac{1}{3}}}$ , in which  $M$  is the molecular weight,  $V$  the molecular volume, and  $T_s$  the melting point of the compound on the absolute scale. Assuming  $k = 3.08 \times 10^{12}$ , this formula has been used to calculate the frequency for a large number of inorganic compounds. The results, which are arranged according to the periodic groups, afford further evidence of the validity of the relation  $N\nu = nv_A$  or  $N\nu = (n + \frac{1}{2})\nu_A$ , according to which the product of the molecular number and the characteristic frequency is a simple multiple of the fundamental frequency  $\nu_A$ .

The fact that this relation holds for compounds which include elements belonging to all the different groups of the periodic system makes it appear very probable that the above equation is the expression of a relation which is of fundamental importance and characteristic of the solid state of matter.

H. M. D.

**Periodic System of the Elements.** CHARLES P. STEINMETZ (*J. Amer. Chem. Soc.*, 1918, 40, 733—739). It is shown that the single, double, and quadruple periodicities which characterise the periodic system can be completely represented by a Riemann surface having two singular points at  $-40$  and  $-130$ . Incidentally, it is pointed out that it is unjustifiable to assume that the functional relation between the properties of the elements and their atomic weights can be represented on a plane.

H. M. D.

**The Ductility of Metals and their Position in the Periodic System.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 247—254; from *Chem. Zentr.*, 1918, i, 509—510).—Lothar Meyer indicated that the ductile elements lie near the maxima and minima of the atomic volume curve. The author regards the occurrence of ductility as dependent on the formation of as many slip-planes as possible in the direction of main extension and the occurrence of movement with as little force as possible, and he uses the term ductility in the commonly accepted sense of capacity to be drawn into wire. Pairs of elements which form a continuous series of mixed crystals are regarded as isomorphous, so that by starting from a known crystal lattice it is possible to find many other examples of the same type. In the periodic system, a certain symmetry prevails in the crystalline form of the typical crystals, but is interrupted by the non-metallic elements of the carbon group. Elements with various crystalline forms are ductile. The ductility is not dependent on any definite space lattice, but probably on the occurrence of only one kind of atoms, between which no valencies are active, in the lattice of their crystals. If the valencies between the atoms of the lattice become active, as in the binary compounds of the metals, the formation of slip-bands is checked and the ductility disappears.

D. F. T.

**The Relationship of the Rare Earths to the Periodic System.** RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1918, 102, 177—200).—The many attempts which have been made to fit the elements of the rare earths into existing groups of the periodic classification have all been unsatisfactory. There is only slight chemical and crystallographic justification for placing lanthanum in the third and cerium in the fourth group, and in any case the valency of an element or the isomorphism displayed by certain of its salts serves as a very uncertain guide to its true relationship to other elements. The author agrees with Tammann that an element should show little or no chemical affinity for another element belonging to the same group; conversely, if two elements form a stable compound, they cannot belong to the same group. When this test is applied to the only rare earth element which is available in sufficient quantity for systematic study, cerium, it must be concluded that this element can belong to none of the ordinary groups of the periodic system. It forms binary compounds with metals of every group, with the exception of those of groups VI and VII, which have not been studied, and many of these compounds are remarkable for their great heats of formation and high melting points. In particular, cerium combines energetically with elements of groups III, IV, and V to form such compounds as  $\text{CeAl}_3$  (m. p.  $1460^\circ$ ),  $\text{CeAl}_4$  (m. p.  $1250^\circ$ ),  $\text{Ce}_2\text{Sn}$  (m. p.  $1400^\circ$ ), and  $\text{Ce}_4\text{Bi}_3$  (m. p.  $1630^\circ$ ), whilst lanthanum also forms with aluminium a strongly exothermic compound,  $\text{LaAl}_4$ , of high melting point.

The new periodic law, based on the atomic numbers of the elements, requires the existence of sixteen elements between Ba(56) and Ta(73). Of these, fourteen rare earth elements are known, one being missing between Nd and Sm, and one between Lu and Ta. Whilst, therefore, the sixteen rare earth elements must form a continuous series with the remaining elements, they must form a special group by themselves.

A satisfactory representation of the position of the rare earth group in the family of elements is obtained in the following manner. The elements are arranged in order of atomic numbers on an ascending spiral, each turn of which corresponds with one short period of eight elements, elements belonging to the same group appearing vertically above one another. After passing Ba, the spiral changes its course and develops a subsidiary, smaller loop which, after making rather more than a complete turn, rejoins the original path of the spiral at Ta, group V. On this subsidiary loop are crowded the sixteen rare earth elements, which form a closely related family independent of the other groups situated on the main spiral. The elements La and Ce appear on the small loop in fairly close proximity to the vertical lines through groups III and IV respectively on the principal spiral, and this may account for certain properties shown by La and Ce in common with the elements of groups III and IV respectively. The rare earth elements themselves exhibit a certain periodicity in their basicity, magnetic properties, and in the solubility of their salts;

such periodicity or gradual change of properties is to be inferred from the form of the loop.

It is further suggested that the triads Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt also form three secondary loops on the principal spiral in place of elements belonging to group VIII. Each triad then forms a sub-group similar in character to the rare earth group, and homologous elements of the three triads appear on vertical lines parallel to the axis of the spiral. It is significant that the typical magnetic elements Fe, Co, Ni, and also the strongly paramagnetic elements Tb, Dy, and Ho, are all among those elements which do not conform to the normal course of the periodic system. E. H. R.

**Gas Generating Apparatus.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, 31, i, 64).—An apparatus for generating small quantities of hydrogen sulphide, carbon dioxide, hydrogen, etc., consists of a wide tube constricted at its middle so as to form two short, cylindrical bulbs; the upper bulb is provided with a tap and contains the ferrous sulphide or calcium carbonate, etc., whilst the lower bulb is connected by a glass tube to an acid reservoir at some height above the bulbs. The whole apparatus is made in one piece. W. P. S.

**Experimental Retort for Dry Distillation.** F. E. COOMBS (*Met. and Chem. Eng.*, 1918, 18, 425).—The retort consists of a cylinder of metal closed at the bottom. A similar cylinder, but of slightly larger diameter, so as to slide loosely over the retort, forms the lid, to which a bent delivery tube is fitted. The lid is secured to the retort by screws. The apparatus is placed in a bath of fused metal or sodium hydroxide, the level of which is below the top of the retort, which is now sealed by the liquid entering the annular space inside the lid. The contents of the retort can be distilled at a known and regulated temperature. The advantage claimed is accessibility for cleaning and charging. H. J. H.

**Extraction Apparatus for the Laboratory.** CARL G. SCHWALBE and WALTER SCHULZ (*Chem. Zeit.*, 1918, 42, 194).—A modification of the Besson extractor (A., 1916, ii, 26) in which no corks are employed and larger quantities (4–6 litres) of material may be extracted. The apparatus consists of a white metal cylinder in the upper part of which is fitted a wire ring which carries a fine cotton bag holding the material to be extracted. Above this bag is fitted a cylindrical condenser, through which a stream of water flows. The apparatus stands in a water-bath heated by a gas burner in the usual manner. All gas- and water-connexions are made of metal so as to ensure the safety of the apparatus. A. B. S.

**Simple Arrangement for Simultaneous Stirring and Filtration.** FRITZ FEIGL (*Zeitsch. angew. Chem.*, 1918, 31, i, 68).—To obviate the errors which occur when portions of a saturated solution at high temperatures are removed for solubility determinations, the author describes a combined stirrer and filter. The apparatus consists of a stout-walled, wide test-tube from which



the bottom has been removed, and on to the sides of which a number of glass vanes have been fastened. One end of the tube is covered with a piece of linen or hardened filter paper, the other end is inserted into a hole in a wooden pulley. The tube is then partly immersed in the saturated solution and rotated; the clear, saturated solution slowly filters into the tube, whence it can be withdrawn in suitable quantities. If a semipermeable membrane is substituted for the filter paper, the apparatus may be used to determine the velocity of diffusion of colloids below their coagulation temperature.

J. F. S.

**Grinding Glass Tips for Drop-weight Apparatus.** EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1918, **40**, 784—785).—For the measurement of surface tension by the drop weight method, it is necessary to prepare capillary tips of circular cross-section by grinding until the section is flat and smooth and the edges are perfectly sharp. To facilitate this, the author recommends the use of Wood's metal or other similar low melting alloy. The glass tube, made ready for the final adjustment of the tip, is lowered into the molten alloy, some of which is drawn into the capillary. The tube is left in position until the alloy has solidified, when the tip becomes firmly embedded in the alloy. The tube and alloy are then ground until the requisite sharp edge is obtained.

H. M. D.

**Willem Homberg.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 602—605).—Further particulars of the life of the alchemist Homberg, including a reproduction of part of an autograph letter (compare this vol., A., ii, 164).

A. J. W.

**Anselmus Boëtius de Boodt.** F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 628—671).—An account of the life and researches of the mineralogist de Boodt, who was born at Bruges in 1550, and died at the same place on June 21st, 1632.

A. J. W.

**Lecture Experiments for Demonstrating the Law of Multiple Proportions.** F. EMICH (*Zeitsch. anal. Chem.*, 1918, **57**, 65—71).—Simple experiments are described, and comprise the estimation of oxygen in cupric and cuprous oxides by reduction with hydrogen, the formation of normal potassium tartrate and potassium hydrogen tartrate, and the gasometric estimation of carbon dioxide in sodium carbonate and sodium hydrogen carbonate.

W. P. S.

**Some Lecture Experiments with Silver Carbide.** [Acetylide]. JOHN EGGERT and HANS SCHIMANK (*Ber.*, 1918, **51**, 454—456. Compare A., 1917, ii, 462).—The experiments are designed to show that pure silver carbide detonates very mildly in a vacuum, its bursting power under ordinary conditions being due to the rapid heating and expansion of the surrounding air.

J. C. W.

## Inorganic Chemistry.

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**The Relation of Iodine to [Sulphur and] Selenium.** E. BECKMANN and C. PLATZMANN (*Zeitsch. anorg. Chem.*, 1918, 102, 215—222).—The molecular weight of iodine determined cryoscopically in sulphur ( $K=213$ ) corresponds with  $I_2$ . Sulphur dissolved in iodine has the molecular composition  $S_8$ , but in the same solvent, selenium is dissociated into  $Se_2$  and  $Se_1$ , although in organic solvents it exists as  $Se_8$ , and iodine, on account of its low dielectric constant, would not be expected to have dissociating properties. The freezing point of sulphur is raised by selenium, as is to be expected, since the two substances are isomorphous. On account of the sparing solubility of selenium in sulphur, experimental determinations were limited to concentrations up to 2.5% Se. Over this range, the elevation of the freezing point was approximately proportional to the concentration, and averaged  $0.242^\circ$  per 1% Se. It is concluded that in sulphur-selenium mixtures the latter is present as  $Se_2$ .

The depression of the freezing point of sulphur-selenium mixtures by iodine and diphenyl was determined. The cryoscopic constants of mixtures containing up to 1.58% Se were found to be practically equal to that of sulphur alone. On the assumption that the change of the freezing point of sulphur containing selenium and iodine is the algebraic sum of the elevation due to  $Se_2$  and the depression due to  $I_2$ , the total effect was calculated and the result compared with the observed value for a number of concentrations. The agreement was generally satisfactory. There is no evidence of the formation of a compound between selenium and iodine, and the low molecular weight of selenium in iodine solution remains unexplained.

E. H. R.

**Action of Thionyl and Sulphuryl Chlorides on Sulphur and Phosphorus.** H. B. NORTH and J. CLAUDE THOMSON (*J. Amer. Chem. Soc.*, 1918, 40, 774—777).—Thionyl and sulphuryl chlorides were heated in sealed glass tubes with sulphur and phosphorus at temperatures ranging from  $70^\circ$  to  $180^\circ$ . Both chlorides react with sulphur at  $150^\circ$  to  $180^\circ$ , with the formation of sulphur dioxide and sulphur monochloride. Under similar conditions, the two chlorides react with both red and yellow phosphorus, with the formation of phosphorus trichloride, according to the equations  $3SO_2Cl_2 + 2P = 2PCl_3 + 3SO_2$ ,  $4SOCl_2 + 2P = 2PCl_3 + 2SO_2 + S_2Cl_2$ . Prolonged heating tends to produce phosphorus pentachloride in accordance with the equations  $PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$ ,  $3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2$ , but these reactions are far from complete after heating for several hours at  $160$ — $180^\circ$  in presence of considerable excess of the sulphuryl or thionyl chloride.

H. M. D.

**Oxidation of Sulphur Dioxide and Ammonia in the Presence of Platinum and Rhodium.** P. WENGER and C. URFER (*Ann. Chim. anal.*, 1918, **23**, 97—104).—Maximum oxidation of sulphur dioxide takes place at 432° in the presence of platinum black, 96·8% of the dioxide being converted into sulphur trioxide. When rhodium black is used as the catalyst, the maximum oxidation (91·1%) occurs at 610°. In the case of ammonia, 97% is converted into nitric and nitrous acids by platinum black at 533° to 562°, whilst with rhodium black a maximum oxidation of 69·7% is attained at 662°.

W. P. S.

**Synthesis of Ammonia at High Temperatures. II.** EDWARD BRADFORD MAXTED (T., 1918, **113**, 386—389. Compare *ibid.*, 168).—Further observations on the combination of nitrogen and hydrogen at high temperatures have been made by passing the 1:3 mixture through a capillary tube fitted with platinum wire electrodes, between which sparks were made to pass by connecting the wires with an induction coil. When the distance between the electrodes is gradually reduced, the ordinary spark discharge is transformed into a small high-tension arc characterised by a continuous flame of high temperature. In experiments in which the rate of passage of the gas was kept constant and the size of the gap reduced, it was found that this was accompanied by a continuous increase in the percentage of ammonia formed. Similar results were obtained when the speed of the gas was controlled so as to give a constant time of contact. For a fixed width of gap, the percentage of ammonia was found to increase as the rate of flow of the gaseous mixture diminished. The results generally are in agreement with those obtained in the previous high-temperature measurements (*loc. cit.*).

H. M. D.

**Synthesis of Nitrosyl Bromide.** E. MOLES (*J. Chim. Phys.*, 1918, **16**, 3—10; *Anal. Fis. Quim.*, 1918, **16**, 377—385). The author has examined the reaction of nitric oxide on bromine, and the nature of the resulting nitrosyl bromide, with the object of ascertaining whether this substance is suitable for use in the determination of the atomic weight of bromine by the method employed by Wourtsel (A., 1913, ii, 771) for chlorine with nitrosyl chloride. After a series of very careful experiments, it is found that the nitrosyl bromide produced always contains a slight excess of bromine, and consequently the compound is of no use for the purpose of determining atomic weights.

J. F. S.

**Preparation of Carbon Tetrachloride from Carbon Disulphide and Chlorine.** ISCO CHEMICAL CO. (U.S. Pats. 1260621 and 1260622).—Carbon disulphide containing free sulphur is treated with chlorine in the presence of a catalyst to form sulphur dichloride and carbon tetrachloride, and an additional quantity of carbon disulphide is then added to convert the sulphur dichloride into sulphur monochloride, with the formation of more carbon

tetrachloride. The product is treated with sufficient tin to convert the sulphur monochloride into sulphur, with the formation of stannic chloride, and, after separating the sulphur, water is added to hydrate the stannic chloride, and the carbon tetrachloride is recovered from the mixture by distillation. A. S.

**Causticising of Potassium Carbonate.** E. BELLONI (*Ann. Chim. Applicata*, 1918, 9, 115—149).—The reaction between potassium carbonate and calcium hydroxide is reversible, and may be represented as a heterogeneous system in which there are two solid phases and one liquid phase containing variable proportions of the other components. From mathematical data based on the consideration of the formulæ of Bodländer and Lucas (A., 1905, ii, 634) and Le Blanc and Novotny (A., 1907, ii, 22), the following general isotherm for the conversion of an alkali carbonate into hydroxide by the action of calcium hydroxide has been deduced:  $C_{\text{KOH(NaOH)}}^0 / C_{\text{K}_2\text{CO}_3(\text{Na}_2\text{CO}_3)} = a - a'\phi + a''\phi^2$ , where  $C_{\text{KOH}}$  represents the concentration in gram-molecules of alkali hydroxide,  $C_{\text{K}_2\text{CO}_3}$  the concentration of the alkali carbonate in the final solution, and  $\phi$  the concentration of the carbonate in the initial solution. The constant  $K$ , which represents any given concentration giving stable equilibrium, is a definite function of  $\phi$  to which the form may be given  $K = a - a'\phi + a''\phi^2$ . In the special case of the conversion of potassium carbonate into hydroxide at  $100^\circ$ , and for values of  $\phi$  varying from 0 to 1.5 (that is, for solutions up to 3*N*), the equation assumes the form  $C_{\text{KOH}}^0 / C_{\text{K}_2\text{CO}_3} = 133.20 - 127.85\phi + 43.50\phi^2$ . The yield of potassium hydroxide obtainable from a solution of potassium carbonate of known concentration may be calculated by means of the equation  $C_{\text{KOH}} = K(-0.25 + \sqrt{0.0625 + \phi/K})$ . At equal molecular concentration of the solutions and under the same conditions of temperature, a greater yield of hydroxide is obtained from sodium carbonate than from potassium carbonate. The formation of a double carbonate of potassium and calcium at a given temperature is only possible at a single definite concentration, which at  $100^\circ$ , the temperature for technical preparation of hydroxide, is 61.78 grams per 100 c.c. This corresponds with a concentration much higher than is used in the manufacturing process. The temperature has a great influence on the velocity of the reaction, but does not affect the final stage of equilibrium. The results for equal concentrations,  $\phi$ , at  $80^\circ$  and  $100^\circ$  were practically identical. [See also *J. Soc. Chem. Ind.*, 363A.] C. A. M.

**Equilibria in Solutions containing Mixtures of Salts.**  
**I. The System Water and the Sulphates and Chlorides of Sodium and Potassium.** W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1918, 10, 344—347).

—The conditions which govern the separation by fractional crystallisation of sodium and potassium salts were investigated by the aid of the phase rule diagrams for such solutions. The equilibrium conditions of the reversible reaction  $3\text{KCl} + 2\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{Na}(\text{SO}_4)_2 + 3\text{NaCl} + 20\text{H}_2\text{O}$  were studied, and the compositions of the solutions

saturated with one or more of these salts at  $0^{\circ}$ ,  $25^{\circ}$ ,  $50^{\circ}$ ,  $75^{\circ}$ , and  $100^{\circ}$  were determined and plotted with respect to four axes representing sodium sulphate, potassium sulphate, potassium chloride, and sodium chloride. The diagrams represent the composition of all possible solutions which can be in equilibrium with these four salts, and with Glauber's salt and sodium potassium sulphate (glaserite), and indicate the stability of glaserite under widely varying conditions. [For details, see *J. Soc. Chem. Ind.*, 369A.]  
W. F. F.

**Separation of Sodium and Potassium Chlorides and Sulphates by Fractional Crystallisation.** W. C. BLASDALE

(*J. Ind. Eng. Chem.*, 1918, 10, 347—353).—The application of the principles described in the preceding abstract to the separation of mixed solutions is shown. Diagrams are given representing the composition of mixed solutions of (1) potassium chloride and sodium chloride, (2) potassium chloride and potassium sulphate, (3) potassium sulphate and sodium sulphate, (4) sodium sulphate and sodium chloride, and (5) mixtures of potassium salts with sulphates and chlorides of sodium and potassium. The diagrams are used to determine possible cycles of operation by which the various salts may be successively crystallised by evaporating and cooling at suitable temperatures. [For details, see *J. Soc. Chem. Ind.*, 369A.]  
W. F. F.

**Production of a Stable Sodium Percarbonate.** HENKEL

& Co. (D.R.-P., 303556, 1915; from *Chem. Zentr.*, 1918, i, 497).—A compound,  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , is obtained by the addition of sodium carbonate to an aqueous solution containing at least a sesquimolecular proportion of hydrogen peroxide; instead of sodium carbonate and hydrogen peroxide being taken as such, these substances may be produced in the solution by a suitable chemical change, for example, from sodium peroxide and sodium hydrogen carbonate.

D. F. T.

**The Calcium Arsenates.** R. H. ROBINSON (*J. Agric. Res.*,

1918, 13, 281—294).—Pure calcium hydrogen arsenate was prepared by pouring a calcium chloride solution slightly acidified with acetic, hydrochloric, or nitric acid into a sodium hydrogen arsenate solution similarly acidified. A heavy, voluminous precipitate was formed, which was washed by decantation, filtered, washed with hot water until free from chlorides, and dried at  $100^{\circ}$ . The washings were evaporated to a small volume, when crystals separated, and were washed and dried. Analysis showed both the powder and crystals to have the formula  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ . The water of crystallisation was lost at  $175^{\circ}$ .

Pure tricalcium arsenate was prepared by pouring an alkaline calcium chloride solution into an alkaline sodium hydrogen arsenate solution. A heavy, voluminous precipitate was formed, which was washed by centrifuging and decantation, and then filtered and

dried at 100°. Analysis agreed with the formula  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The water of crystallisation was lost at 175°.

The specific gravity of the salts was determined by weighing in specially dehydrated absolute alcohol at 20°. The results were: for  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ ,  $D_4^{20}$  3.09; for  $\text{CaHAsO}_4$ , 3.48; for  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , 3.33; for  $\text{Ca}_3(\text{AsO}_4)_2$ , 3.31. Solubility was determined at 25° in a water-bath fitted with a revolving bottle-holder. One hundred grams of the solution contained in the case of  $\text{CaHAsO}_4$  0.3108 gram of the salt, and in the case of  $\text{Ca}_3(\text{AsO}_4)_2$  0.0133 gram.

J. H. J.

**An Artificial Patina.** OTTO GROTIAN (*Zeitsch. Elektrochem.*, 1918, 24, 83).—The author describes a method of artificially producing an incrustation or patina on copper articles similar to that found on ancient bronzes. This film is produced by electrolysing a solution of copper sulphate between copper electrodes for three minutes with a current density of 1 amp./per sq. decimetre; the current is then interrupted and the cathode removed from the liquid. The anode is allowed to remain undisturbed in the liquid for twenty-four hours. The process is repeated several times, alternately passing the current for three minutes and leaving the anode for twenty-four hours. After several repetitions, the anode is removed and found to be covered with a beautiful bluish-green, non-crystalline patina, which cannot be removed by washing. On analysis, the film is shown to have the composition  $\text{CuO} \cdot 3\text{H}_2\text{O}$ .

J. F. S.

**Mercury Fulminate and its Estimation.** G. S. HEAVEN (*J. Soc. Chem. Ind.*, 1918, 37, 143—147r).—Commercial mercury fulminate consists of a crystalline powder varying in colour from pale cream to dark brown; the largest crystals do not exceed 1 mm. in length, and these are more sensitive to impact than are the smaller crystals. A very fine powder, sifted through calico, fails to fire. Fulminate is soluble in alcohol, ammonia, pyridine, potassium cyanide solution, and in cold water, but is decomposed by hot water, alkali solutions, and thiosulphate solution. It does not inhibit the growth of fungi; *Tricoderma viride* and *Acrostagmus albus* Preuss grow readily on bags containing fulminate, and even on the crystals themselves. The following method is recommended for the analysis of detonator composition containing fulminate, antimony sulphide, potassium chlorate, etc. A quantity of 0.3 gram of the sample is treated with 50 c.c. of *N*/10-thio-sulphate solution, 0.3 gram of boric acid is added, the mixture is stirred for three minutes, and then titrated with sulphuric acid, using methyl-orange as indicator. The sulphuric acid is standardised previously against pure mercury fulminate. Any antimony sulphide which may be present is then collected on a filter, washed, dried, and weighed, or estimated volumetrically if the sample contains powdered glass. To the filtrate are added 100 c.c. of 10% ferrous sulphate solution containing 1 c.c. of free sulphuric acid,

the mixture is boiled for thirty minutes, the mercury sulphide collected, dissolved in aqua regia, the solution neutralised with ammonia, acidified with hydrochloric acid, and the mercury precipitated as sulphide. The mercury sulphide is collected and weighed, and the filtrate, containing reduced chlorate, is oxidised with nitric acid, and the chloride estimated volumetrically.

W. P. S.

**Preparation of Inorganic Stannichlorides.** J. G. F. DRUCE (*Chem. News*, 1918, 117, 193—196).—A number of stannous and stannic chlorides of uni- and bi-valent metals have been prepared. The stannochlorides were obtained by crystallisation of acid solutions containing stannous chloride and the chloride of the second metal. To obtain the stannichlorides, these solutions were first subjected to the action of chlorine. The recorded analyses of the products, in which the water of crystallisation was obtained by difference, show that magnesium and zinc yield anhydrous stannochlorides, whilst those formed by potassium and ammonium contain two molecules of water of crystallisation. The data for the stannichlorides correspond with the following formulae:  $\text{Li}_2\text{SnCl}_6 \cdot 8\text{H}_2\text{O}$ ;  $\text{Na}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$ ;  $\text{K}_2\text{SnCl}_6$ ;  $\text{Rb}_2\text{SnCl}_6$ ;

$(\text{NH}_4)_2\text{SnCl}_6$ ;  
 $\text{CaSnCl}_6$ ;  $\text{SrSnCl}_6 \cdot 4\text{H}_2\text{O}$ ;  $\text{MgSnCl}_6 \cdot 6\text{H}_2\text{O}$ ;  $\text{ZnSnCl}_6 \cdot 6\text{H}_2\text{O}$ ;  
 $\text{CdSnCl}_6$ ;  $\text{CoSnCl}_6 \cdot 6\text{H}_2\text{O}$ ;  $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$ .

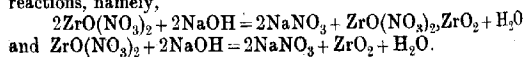
The anhydrous potassium, rubidium, and ammonium stannic chlorides are quite stable in the air and do not deliquesce. The alkaline earth stannochlorides are entirely deliquescent, and on this account it was found impossible to obtain a pure specimen of the barium salt.

H. M. D.

**Normal Zirconyl Nitrate.** ED. CHAUVENET and (MLLE.) L. NICOLLE (*Compt. rend.*, 1918, 166, 781—783).—The authors were unable to confirm the existence of a normal zirconium nitrate  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , commonly described in text-books. By evaporating a solution of zirconium hydroxide in nitric acid, even in an atmosphere saturated with nitric acid fumes, they always obtained a zirconyl nitrate,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , or at temperatures below 10° the hydrate,  $\text{ZrO}(\text{NO}_3)_2 \cdot 3 \cdot 5\text{H}_2\text{O}$ . Attempts to prepare the anhydrous nitrate were not successful, the dehydration being always accompanied by loss of nitric acid.

W. G.

**Basic Zirconyl Nitrates.** ED. CHAUVENET and (MLLE.) L. NICOLLE (*Compt. rend.*, 1918, 166, 821—824).—Zirconyl nitrate  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (compare preceding abstract), when dissolved in water, slowly undergoes hydrolysis, and there is slow formation of a precipitate having the composition  $\text{ZrO}(\text{NO}_3)_2 \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$ . A study of the neutralisation by *N*/100-sodium hydroxide of the nitric acid formed during the hydrolysis showed that there are two reactions, namely,



When the normal zirconyl nitrate is heated at  $120^{\circ}$  in the presence of nitric acid vapour, it undergoes dehydration, and at the same time loss of nitric acid, giving a *basic nitrate*,  $3\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ . If the dehydration takes place in air, there are formed the following basic nitrates: at  $110^{\circ}$ ,  $2\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ ; at  $150^{\circ}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{ZrO}_3 \cdot 4\text{H}_2\text{O}$ ; at  $215^{\circ}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{ZrO}_2 \cdot 5\text{H}_2\text{O}$ ; and at  $250^{\circ}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 10\text{ZrO}_3 \cdot 4\text{H}_2\text{O}$ , and above this temperature zirconium oxide is formed. W. G.

**The Resistance Limits of Mixed Crystals of Vanadium and Silicon with Iron.** G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 161—179; from *Chem. Zentr.*, 1918, i, 510).—The “resistance limit” is the term given to the composition of mixed crystals at which a sudden alteration occurs in the susceptibility to chemical agents. Whereas it is possible to observe in a direct manner the alterations in the surface of polished pieces of alloys consisting of copper-gold or silver-gold mixed crystals, this cannot be done in the present case, and it is necessary to observe, instead, the effect of various reagents on the metal. After ordinary, slow cooling, mixed crystals of iron and vanadium containing up to 74% molecule of the latter are ferromagnetic, whilst mixed crystals richer in vanadium are inactive. Examination was made of the behaviour of the mixed crystals towards solutions of various salts and acids, the resistance limit being found at  $0.50 \pm 0.05$  mol. vanadium.

The iron-silicon mixed crystals gave rather irregular results; solutions of metallic nitrates cause the iron in the mixed crystals to become passive; the action of acids is also somewhat abnormal; copper sulphate, mercuric chloride, gold chloride, and several other salts, together with iodine, indicate a resistance limit at 0.25 mol. silicon, which appears to confirm the existence of the compound  $\text{FeSi}$ . D. F. T.

## Mineralogical Chemistry.

**The Old and the New Mineralogy.** SIR HENRY ALEXANDER MEYER (*T.*, 1918, 113, 363—386).—A lecture delivered before the Chemical Society on April 18th, 1918. II. M. D.

**Chemical Composition of Melanophlogites.** E. MANZELLA (*Ann. Chim. Applicata*, 1918, 9, 91—101. Compare Lasaulx, this Journal, 1876, ii, 54; Bertrand, A., 1881, 1000).—Melanophlogite, a mineral discovered by Lasaulx in association with certain specimens of sulphur, is characterised by its behaviour on heating, changing successively in colour to greyish-yellow, greyish-blue, and deep bluish-black. Purified specimens of various origin recently



examined had the following composition: hydrogen, 1.47 to 1.56; carbon, 3.32 to 3.91; silica, 88.76 to 89.12 sulphuric anhydride, 0.63 to 2.49; iron and loss, 0.27 to 0.60; and substances undetermined, 2.67 to 4.94%. A decrease in the proportion of sulphuric anhydride was accompanied by a reduction in the degree of blackening on heating, but other experiments showed that the alteration in colour must be attributed solely to carbonisation of the organic constituents in the mineral.

C. A. M.

### Analytical Chemistry.

**Acidimetry of Coloured Solutions. An Application of the Pocket Spectroscope.** ALFRED TINGLE (J. Soc. Chem. Ind., 1918, 37, 117; J. Amer. Chem. Soc., 1918, 40, 873-879).—A method is described whereby highly coloured acid solutions may be accurately titrated. The process depends on the fact that the absorption spectra of indicators are different in acid and in alkaline solutions. To make a determination, two similar vessels are taken, one of which contains the solution to be titrated and the other an equal volume of distilled water. To the latter, one drop of standard alkali is added, and then the indicator is slowly added from a burette until the characteristic absorption band shows a sufficiently sharp edge. The position of this edge is noted. Then the same volume of indicator is added to the solution to be estimated, and alkali added from a burette until the characteristic band is observed in the same position. This gives the end-point of the titration. The change does not involve the appearance of a new absorption band, but rather the shifting of a band already present. The method was tested on solutions of sulphuric acid of known concentration, which were coloured by the addition of neutral tea extract or liquorice. The results are quite as accurate as those obtained for colourless solutions by the ordinary method. The amount of indicator used is rather larger than that generally employed; the exact amount necessary must be found experimentally. In the present experiments, 1 c.c. of methyl-orange and 2.5 c.c. of cochineal extract were used.

J. F. S.

**Mercuric Oxide as a Standard for Volumetric Analysis.** L. ROSENTHALER (Zeitsch. anal. Chem., 1918, 57, 98).—Inze has recommended the use of yellow mercuric oxide as a standard in volumetric analysis (A., 1917, ii, 327), but the author points out that he and Abelmann had previously used mercuric oxide for the purpose (A., 1913, ii, 786).

W. P. S.

**Detection of Anions.** FRITZ FEIGL (Zeitsch. anal. Chem., 1918, 57, 135-138).—The substance is boiled with concentrated sodium

carbonate solution or fused with a mixture of sodium and potassium carbonates; after filtration, the solution is nearly neutralised with nitric acid and warmed with the addition of an excess of solid zinc nitrate. The mixture is filtered; the precipitate contains zinc sulphide, sulphite, phosphate, borate, fluoride, ferrocyanide, ferricyanide, and cyanide, and also molybdate, vanadate, and tungstate, whilst the filtrate contains zinc thiocyanate, chloride, bromide, iodide, sulphate, thiosulphate, and sulphite. These substances are then identified by drop reactions without further separation [See also *J. Soc. Chem. Ind.*, July.]

W. P. S.

**Estimation of Chlorine in Organic Substances (Gastric Juice, Blood, Milk, etc.).** SIBOT and JORET (*Ann. Chim. anal.*, 1918, **23**, 109—113).—The total chlorine in gastric juice is estimated by Volhard's method after the sample has been treated with Esbach's reagent (10 grams of picric acid and 25 grams of acetic acid per litre of water) and filtered. Chlorine in organic and inorganic combination is estimated in the same way after the sample has been evaporated to expel free hydrochloric acid, whilst chlorine in inorganic combination is obtained by titrating the residue left after evaporation and incineration. In the case of blood, sodium metaphosphate is recommended as a clarifier; 20 c.c. of the blood are mixed with 75 c.c. of water, 10 drops of nitric acid, 20 c.c. of 5% sodium metaphosphate solution, and 1.5 c.c. of acetic acid. The mixture is then diluted to 200 c.c., filtered, and the chlorine titrated in the filtrate. The acetic acid-picric acid solution may be used for precipitating the casein, etc., in milk previous to the estimation of the chlorine present.

W. P. S.

**Gravimetric Analysis. V. [Chlorides, Bromides, and Iodides.]** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 101—103).—Chlorides, bromides, and iodides are precipitated by a small excess of *N*-silver nitrate in 100 c.c. of the cold solution to which has been added 5 c.c. of *N*-nitric acid, or, in presence of ferric salts, 10—20 c.c. In the case of chlorides and bromides, the mixture is left for one hour and then boiled; in the case of iodides, the silver is added first, the nitric acid after half an hour, and the mixture is boiled after another half-hour. Twenty-four hours later, the precipitate is collected on a plug of cotton wool in a Kelm funnel and dried at 132°. It is washed with 50 c.c. of water acidified with nitric acid, and later with 50 c.c. acidified with acetic acid. Correction values amounting to a few tenths of a mg., according to the weight of the precipitate, are used to improve the accuracy of the results. Iodides may also be precipitated in the presence of hydrochloric acid as palladium iodide. 0.5 Gram of palladium is dissolved in nitric acid and the solution evaporated to dryness several times with hydrochloric acid; the residue is taken up with 10 c.c. of 10% hydrochloric acid, 1 c.c. of alcohol is added to remove any free chlorine, and the solution made up to 100 c.c. In absence of chlorides, the palladium iodide

remains in colloidal solution; when precipitated cold, it is flocculent, and becomes granular on heating. With a preponderating quantity of iodide, the neutral solution is diluted so that 100 c.c. will give about 0.1 gram of precipitate; 1.0 gram of sodium chloride is added, and 10 c.c. of palladium chloride solution, with agitation. The liquid is heated until the precipitate becomes granular, and the latter is collected on the cotton filter after twenty-four hours, washed with 100 c.c. of cold water, and dried at 132°. With small quantities of iodide, 100 c.c. of the liquid are acidified with hydrochloric acid and precipitated with 1 c.c. of the palladium solution in the cold. The precipitate is allowed to remain for twenty-four or forty-eight hours, according to its quantity, and is collected in the flocculent condition. The palladium iodide is somewhat soluble in presence of alkali bromides; in presence of large quantities of chlorides, a small correction is applied.

J. F. B.

**Titration Method for Chlorine, Bromine, Cyanogen, and Mercury.** EMIL VOTOČEK (*Chem. Zeit.*, 1918, 42, 257—260).—Chlorides may be titrated with standardised mercuric nitrate solution in the presence of a small quantity of nitric acid; 0.06 gram of crystallised sodium nitroprusside is used as the indicator, and the volume of the solution should be about 250 c.c. Sulphates, phosphates, and chlorates do not interfere, but sulphites and nitrites must not be present. The method is trustworthy and more accurate than Volhard's method. [See further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

**The Estimation and Distribution of Bromine in the Organs and in the Blood after Dosing with Sodium Bromide.** W. AUTENRIETH (*Munch. med. Woch.*, 1918, 65, 33—35; from *Chem. Zentr.*, 1918, i, 472—473).—Bromine in bromides of the alkali metals can be estimated colorimetrically by treating the acidified aqueous solution with potassium hydrogen sulphate and potassium permanganate, the liberated bromine being extracted with chloroform and the extract compared with a standard bromine solution, using the Autenrieth-Königsberger colorimeter. The method is not affected by the presence of chlorine and is especially suitable for small quantities. Organs such as liver, kidneys, brain, etc., are heated in a nickel crucible with pure sodium hydroxide and a little potassium nitrate, and the acidified solution treated in the manner described. Sodium bromide is retained tenaciously by the human organism, and only very slowly eliminated by the kidneys, its retention being favoured by a diet poor in chlorine. The brain shows no specific attraction for bromine.

D. F. T.

**Gravimetric and Volumetric Estimation of Fluorine Precipitated as Thorium Fluoride.** F. A. GOOCH and MATSUKE KOBAYASHI (*Amer. J. Sci.*, 1918, [iv], 45, 370—376).—Investigation of the method described by Pisani (*A.*, 1916, ii, 393)

showed that the acidity of the solution and the excess of precipitant are important factors in the estimation of fluorine as thorium fluoride. The acidity of the solution (as free acetic acid) should be from  $N/50$  to  $N/5$ , and the quantity of thorium added should not exceed by more than 50% the amount required for the precipitation. The thorium fluoride may be collected and ignited to oxide, the latter being taken as a measure of the thorium fluoride,  $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ , or the excess of thorium, after filtration, may be precipitated as oxalate and this titrated with permanganate solution (compare this vol., ii, 177). [See, further, *J. Soc. Chem. Ind.*, 391A.] W. P. S.

**Time as a Factor in Gravimetric Analysis. I. Precipitation of Sulphuric Acid.** Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, 57, 77—98).—In the precipitation of sulphuric acid as barium sulphate, the rate at which the barium chloride solution is added has a considerable influence; the most trustworthy results are obtained when the addition is extended over a period of not less than 1.5 minutes. The concentration of the solutions, stirring, concentration of hydrochloric acid, etc., also have an influence, but temperature has little effect. The presence of potassium chloride decreases the amount of barium sulphate found, and to some extent counterbalances the effect of rapid precipitation, but this compensation depends on definite conditions of experiment. W. P. S.

**The Estimation of Sulphates in Urine.** A. L. FLOHR (*Arch. Néerland. physiol.*, 1918, 2, 346—351).—The benzidine method of Rosenheim and Drummond for estimating inorganic and ethereal sulphates gives satisfactory results. If the liquid becomes coloured after hydrolysis of the ethereal sulphates by hydrochloric acid, and the colour interferes with the titration, it can be removed sufficiently by treating the liquid with animal charcoal. S. B. S.

**Estimation of Non-protein Nitrogen in Blood.** ISIDOR GREENWALD (*J. Biol. Chem.*, 1918, 34, 97—101).—A full account of work previously published (*A.*, 1917, ii, 523). H. W. B.

**New Method for the Direct Nesslerisation of Ammonia in Urine.** JAMES B. SUMNER (*J. Biol. Chem.*, 1918, 34, 37—41).—In the Folin and Denis direct Nesslerisation method (*A.*, 1916, ii, 574), the Merck's blood charcoal may be replaced by copper sulphate. The urine is treated with a practically saturated solution of copper sulphate (298 grams of the crystallised salt per litre). Copper hydroxide is then precipitated by adding a 2.03*N*-sodium hydroxide solution until the neutral point is almost reached, when about 90% of the creatinine is also precipitated. The small amount of creatinine remaining in solution is not sufficient to interfere with the subsequent Nesslerisation.

For rough comparative tests, standard colours similar to those

obtained by Nesslerisation are prepared by dilution of a solution containing 6% of crystallised ferric chloride and 2.5% of crystallised cobalt nitrate.

H. W. B.

**Apparatus for the Estimation of Nitric Acid by the Schulze-Tiemann Method.** KARL LEUCHS (*Chem. Zeit.*, 1918, **42**, 235).—The decomposition flask is closed with a glass stopper provided with a tapped funnel and a delivery tube, and the stopper is surrounded by a water-seal. The delivery tube, which is bent downwards and under the lower end of the gas-collecting burette, is provided with a glass non-return valve. The whole apparatus is constructed of glass.

W. P. S.

**Gasometric Estimation of Nitrates.** C. A. HILL (*Analyst*, 1918, **43**, 215–216).—When an external reaction bottle is used in the estimation of nitrates by shaking the latter with sulphuric acid and mercury, it is necessary to fill the bottle previously with a gas inert towards nitric oxide. Carbon monoxide may be used for this purpose, and is prepared by heating a mixture of sodium formate and concentrated sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

**New Volumetric Method for the Estimation of Phosphates in Urines.** ARGEO ANGIOLANI (*Giorn. Farm. Chim.*, 1917, **66**, 251–252; from *Chem. Zentr.*, 1918, **j**, 571).—Twenty-five c.c. of the urine are treated with 1 c.c. of 20% hydrochloric acid, 1 gram of ammonium chloride, and 10 c.c. of a citric acid–magnesium solution (a solution of 35 grams of magnesium oxide in 260 grams of citric acid, the total bulk being 500 c.c., which is then treated with 400 c.c. of 10% ammonia solution and kept for two hours). The precipitate is collected, washed with very dilute ammonia solution, dried at 30–40°, and then dissolved in 50 c.c. of N/10-sulphuric acid, of which the excess is then titrated with N/10-sodium hydroxide solution, using methyl-orange as indicator. One c.c. of N/10-acid is equivalent to 3.55 mg.  $P_2O_5$ .

D. F. T.

**Marsh's Apparatus.** W. KIRKBY (*Pharm. J.*, 1918, **100**, 286).—A tube loosely packed with cotton wool is interposed between the generating flask and the hydrogen jet with the object of preventing any risk of explosion.

C. A. M.

**Simple Process for the Estimation of Small Quantities of Arsenic in Corpses.** H. FÜHNER (*Ber. Dent. Pharm. Ges.*, 1918, **28**, 221–229).—The process consists in the destruction of the animal matter by permanganate and sulphuric acid, the distillation of the solution with sodium chloride, and the estimation of the arsenic in the distillate by the Gutzeit method, using mercuric bromide paper. [See *J. Soc. Chem. Ind.*, July.]

J. H. J.

**Estimation of Carbon Dioxide in Carbonates by Pittrich's Method.** BÉLA VON HORVATH (*Chem. Zeit.*, 1918, **42**, 121).—Carbon dioxide may be estimated in sodium carbonate or barium carbonate by heating the same at dull redness with borax which has been heated previously at  $1000^{\circ}$ ; the carbonate is decomposed readily, and the loss in weight gives the amount of carbon dioxide present. [See, further, *J. Soc. Chem. Ind.*, 369A.]  
W. P. S.

**Filtration of Silica.** P. NICOLARDOT and J. KOENIG (*Ann. Chim. anal.*, 1918, **23**, 104–109).—The fact that a minute quantity of silica passes into the filtrate when hydrated silica is evaporated to dryness and then collected on a filter does not appear to be due to solubility of the silica; the effect of successive evaporations and heating at  $110^{\circ}$  is to agglomerate the silica so that the whole of it is retained by a good filter. It is recommended that the silica be twice evaporated with hydrochloric acid and heated at  $110^{\circ}$ , but without intervening filtration, before it is collected; the filtrate may be passed once more through the filter. [See, further, *J. Soc. Chem. Ind.*, July.]  
W. P. S.

**Estimation of Strontium.** L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 80 and 83–84).—*As Sulphate.*—One hundred c.c. of a neutral solution containing 0.5 gram of strontium salt are acidified with 1 c.c. of acetic acid, heated to the boiling point, and 10 c.c. of a 10% solution of sodium sulphate are added. Heating is continued until the precipitate is powdery, when it is left overnight. It is transferred to a Gooch crucible, washed with 50 c.c. of saturated strontium sulphate solution, and weighed after drying at  $132^{\circ}$ . If the filtrate is required further, alcohol is used as the washing agent. The presence of other salts, especially magnesium chloride and hydrochloric and nitric acids, leads to low results.

*As Carbonate.*—1.0 Gram of potassium nitrate and 10 c.c. of 10% sodium carbonate solution are added to a boiling solution of not more than 0.5 gram of strontium salt in 100 c.c. of solution. Next day the precipitate is washed with 50 c.c. of saturated strontium carbonate solution and weighed as  $\text{SrCO}_3$  after drying at  $132^{\circ}$ . Owing to incomplete loss of carbon dioxide on ignition, the precipitate cannot be weighed as oxide.

*As Oxalate.*—The precipitation is made with 10% solution of potassium oxalate, and resembles that of the sulphate. After remaining overnight, the precipitate is washed with saturated strontium oxalate solution. It is dried at  $100^{\circ}$  for two hours and weighed as  $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , or at  $132^{\circ}$  for six hours and weighed as  $\text{SrC}_2\text{O}_4$ . Other salts, especially magnesium chloride, interfere. This is the most convenient and exact method of estimating strontium.  
H. J. H.

**Time as a Factor in Gravimetric Analysis. Precipitation of Barium Chloride with Sulphuric Acid.** Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, **57**, 113–121).—In the gravi-

metric estimation of barium as barium sulphate, sulphuric acid should be used for the precipitation; alkali sulphates must not be used. The acid should be added rapidly; if it is added slowly, the results obtained are too low. [See, further, *J. Soc. Chem. Ind.*, 352A.] W. P. S.

**Volumetric Estimation of Lead by means of Ammonium Molybdate.** LINDT (*Zeitsch. anal. Chem.*, 1918, 57, 71—76).—In this process, it is essential that an excess of ammonium acetate should be avoided in dissolving the lead sulphate; the results obtained are too high in the presence of such excess, but are trustworthy when the lead sulphate is dissolved in the minimum requisite quantity of the acetate solution. [See, further, *J. Soc. Chem. Ind.*, 352A.] W. P. S.

**Estimation of Copper as Copper Oxide after previous Precipitation as Thiocyanate.** G. FENNER and J. FÖRSCHMANN (*Chem. Zeit.*, 1918, 42, 205—206).—The inconvenient drying of the cuprous thiocyanate precipitate to constant weight is unnecessary, and may be avoided by conversion of the precipitate into cupric oxide by roasting in a muffle at a temperature near 800°. [See also *J. Soc. Chem. Ind.*, 391A.] D. F. T.

**Analysis of White Metal.** F. KUREK and A. FLATH (*Chem. Zeit.*, 1918, 42, 133—134).—Tin is estimated by dissolving the alloy in hydrochloric acid with the addition of ferric chloride, reducing the tin with metallic iron, separating the precipitated antimony and copper, and titrating the filtrate with ferric chloride solution. The antimony and copper are then dissolved in hydrochloric acid to which potassium chlorate is added, excess of free chlorine is expelled by boiling the solution, the two metals are separated as their sulphides, the antimony sulphide is dissolved in sodium sulphide solution, again precipitated in the presence of an excess of oxalic acid, dissolved in hydrochloric acid, the solution boiled until the antimony is reduced, and then titrated with potassium bromate solution. Suitable methods are also described for the estimation of lead, copper, iron, aluminium, nickel, and zinc in the alloy. [See, further, *J. Soc. Chem. Ind.*, 877A.] W. P. S.

**Use of Metallic Silver as a Reducing Agent in the Volumetric Estimation of Iron.** GRAHAM EDGAR and A. R. KEMP (*J. Amer. Chem. Soc.*, 1918, 40, 777—784).—The reaction between metallic silver and solutions of ferric sulphate in the presence of sulphuric acid and a soluble thiocyanate has been examined. The results obtained show that silver may be employed to effect the complete reduction of the ferric salt provided the dissolved silver is precipitated by thiocyanate. The resulting ferrous solution is filtered, treated with an excess of silver nitrate, and titrated with potassium permanganate. An alternative

method consists in titrating the excess of silver nitrate with standard thiocyanate.

The thiocyanate serves to show when the reduction is complete, and further advantages of the method are that silver is usually quite free from iron, that it does not reduce titanium at all, and that it reduces vanadium quantitatively to the quadrivalent condition. [Compare *J. Soc. Chem. Ind.*, 391A.] H. M. D.

**Estimation of Iron in Lactic Acid.** A. HARVEY (*J. Soc. Leather Trades' Chem.*, 1918, 2, 37—38).—Iron in lactic acid can be estimated very exactly by a colorimetric method in which the colour developed with potassium ferrocyanide is matched against the colour produced by standard iron solution. Potassium thiocyanate is useless. F. C. T.

**Quantitative Separation of Iron from the Cerite Metals in the presence of Calcium.** A. WÖBER (*Zeitsch. landw. Versuchsw. Oesterr.*, 1917, 20, 500—501; from *Chem. Zentr.*, 1918, i, 476).—A weighed sample is dissolved by prolonged treatment with 2% hydrochloric acid, and to an aliquot portion of the solution there is added tartaric acid in the proportion of approximately four grams to one of the substance. On saturating the solution with hydrogen sulphide and adding aqueous ammonia until a pure black precipitate of iron sulphide is obtained, the transiently precipitated hydroxides of the cerite metals are redissolved. The iron sulphide is treated in the usual manner, whilst the estimation of the cerite metals is effected by the method of Hauser and Wirth (A., 1908, ii, 778). D. F. T.

**Estimation of Nickel with  $\alpha$ -Benzildioxime.** R. STREBINGER (*Chem. Zeit.*, 1918, 42, 242—243).—The author agrees with Grossmann and Mannheim (A., 1917, ii, 391) that Atack's method of estimating nickel by precipitation with  $\alpha$ -benzildioxime is trustworthy for small quantities of the metal. When, however, the quantity of nickel exceeds 0.025 gram, the precipitate contains a certain amount of occluded  $\alpha$ -benzildioxime, and the results obtained are too high. In such cases, the precipitate should be ignited and the resulting nickel oxide weighed. W. P. S.

**Estimation of Chromium in Chromium Salts, Chrome Liquors, Leather Ashes, and Chromium Residues.** KARL SCHORLEMMER (*Collegium*, 1917, 345 and 371; from *Chem. Zentr.*, 1918, i, 377—378).—The solution of the chromium salt is treated cautiously with approximately *N*-sodium hydroxide until the precipitate has redissolved. Aqueous hydrogen peroxide of approximately 3% concentration is then added, and the solution is boiled until no more oxygen is liberated. The resulting solution is acidified with sulphuric acid, and the amount of chromate estimated by one of the usual volumetric methods. Leather ash or dry



chromium residues should be mixed with anhydrous sodium carbonate and magnesium oxide and roasted until yellow, the aqueous extract then being titrated after acidification. For the oxidation of solutions of very impure chromium salts, it is better to use alkaline potassium permanganate solution. The presence of iron in the ash of chrome leather may interfere with the chromium estimation.

D. F. T.

**Estimation of Molybdenum.** O. BINDER (*Chem. Zeit.*, 1918, **42**, 255).—When molybdenum is precipitated as sulphide and the latter then ignited to oxide, the oxidation is not complete unless the substance, after preliminary ignition, is treated with nitric acid, evaporated, dissolved in ammonia, reprecipitated with nitric acid, evaporated, and ignited. A correction must be made for any traces of matter which remain insoluble when the ignited oxide is dissolved in ammonia. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

**The Estimation of Molybdenum as Lead Molybdate.** ROBERT STREIBINGER (*Oesterr. Chem. Zeit.*, 1917, [ii], **20**, 226—228; from *Chem. Zentr.*, 1918, i, 378).—For the estimation of molybdenum in ferro-molybdenum, 0.5—1 gram is fused with 10 grams of sodium peroxide in an iron crucible. The product is extracted with 500 c.c. of water, and 100 c.c. are taken for the test; after the removal of any iron by the addition of nitric acid and then ammonia solution, the solution is neutralised with acetic acid, boiled, and treated successively with solutions of lead acetate (2–5 grams) with acetic acid (2 c.c.) in 30 c.c. of water, and ammonium acetate (10 grams) in 50 c.c. of water. After boiling for a short time, the precipitate is allowed to settle for six hours. The precipitate is removed by filtration, washed with dilute ammonium acetate solution, dissolved in diluted nitric acid, and reprecipitated by the addition of a solution of ammonium acetate (10 grams) in 50 c.c. of very dilute acetic acid. After twelve hours, the lead molybdate is again separated, washed, dried, and ignited at a moderate temperature before final weighing as  $\text{PbMoO}_4$ .

D. F. T.

**A Colour Reaction of Thorium and Zirconium with Pyrogallolaldehyde.** H. KASERER (*Chem. Zeit.*, 1918, **42**, 170).—On the addition of an aqueous solution of pyrogallolaldehyde to one of a thorium compound, a yellow colour is formed, and, after a time, a dirty yellow precipitate is produced, which when filtered off leaves a colourless filtrate. Zirconium compounds, after boiling or after the addition of hydrogen peroxide, give a similar colour and precipitate with cerium compounds; the yellow colour remains after boiling. In the presence of nitric, sulphuric, or hydrochloric acid, a colourless solution and no precipitate are produced. A solution containing only 0.1 mg. of thorium nitrate per 100 c.c. shows the colour† clearly. Pyrogallol, pyrogallolcarboxylic acid, and protocatechualdehyde do not give this reaction.

The pyrogallolaldehyde is prepared by dissolving 38 grams of pyrogallol and 36.3 grams of formanilide in absolute ether, condensing this with 15.2 grams of phosphoryl chloride, and filtering after twelve hours. The residue is dissolved in alcohol and precipitated by sodium chloride. The crystals are treated with warm sodium hydroxide, a current of hydrogen is passed through the solution, after which it is acidified and the aldehyde extracted with ether and purified by conversion into the bisulphite compound.

A. B. S.

**Graphic Methods of Analysis.** HANS GRADENWITZ (*Chem. Zeit.*, 1918, **42**, 221).—The composition of such mixtures as formaldehyde, methyl alcohol, and water, and ethyl acetate, alcohol, and water, may be found from the graphs given, the data to be determined being, in the first case, the specific gravity and the formaldehyde content, and in the second, the specific gravity and the ethyl acetate content. [See, further, *J. Soc. Chem. Ind.*, 392A.]

W. P. S.

**Method for Detecting Small Quantities of Chloretone (Trichloro-*tert.*-butyl Alcohol) in Aqueous Solutions.** T. B. ALDRICH (*J. Biol. Chem.*, 1918, **34**, 263—267).—The solution containing the chloretone is subjected to steam distillation. If a large amount of chloretone is present, it crystallises in the cooler part of the condenser in needles. When only small amounts of chloretone are present, crystallisation may not occur, but if the distillate is placed in a small flask fitted with a reflux condenser and boiled for half an hour, needle crystals are then obtained in the condenser when the amount of chloretone exceeds 0.25 mg. If protein is present, it should be digested with pepsin and hydrochloric acid before the steam distillation is carried out. The presence of other organic solvents prevents the crystallisation, and thus interferes with the recognition of chloretone by this method.

H. W. B.

**Estimation of Cholesterol in Blood.** L. KAST, V. C. MYERS, and EMMA L. WARDELL (*Proc. Soc. Exp. Biol. Med.*, 1917, **15**, 1—2; from *Physiol. Abstr.*, 1918, **3**, 31).—One c.c. of blood is extracted with chloroform, and in the extract the cholesterol is estimated colorimetrically by the Liebermann-Burchard reaction (compare *Physiol. Abstr.*, 1917, **2**, 675). The values obtained are lower than those of Bloor, but are believed to be more accurate.

W. G.

**Cambridge's Method for the Estimation of [Reducing] Sugar in Urine.** R. W. GARROW (*Pharm. J.*, 1918, **100**, 148—149).—In estimating sugar by this method (*A.*, 1917, ii, 276), it is noticed in titrating back the excess of iodine with thio-sulphate that up to the point where the blue starch iodide is discharged the solution is transparent, but immediately after the first end-point is reached a slight opalescence begins to appear, in-

creasing to a white precipitate of cuprous iodide, and the blue colour returns. The first discharge of the blue colour should be taken as the end-point, and the titration should be done as rapidly as possible. [See, further, *J. Soc. Chem. Ind.*, 276A.]

J. F. B.

**Polarimetric Estimation of Dextrose in Urine.** G. FRERICHS and E. MANNHEIM (*Apoth. Zeit.*, **33**, 34; from *Chem. Zentr.*, 1918, i, 380. Compare A., 1917, ii, 393).—A 100 c.c. flask containing 5 c.c. of lead acetate solution is filled to the mark with the urine and shaken well; the liquid is then filtered and examined in the polarimeter in a 2-dm. tube, the rotation giving the content of anhydrous dextrose in grams per 100 c.c. of urine. The lead acetate solution should contain 10 grams of the salt and 5 grams of 30% acetic acid in 20 grams of water. If the lead acetate treatment fails to decolorise the urine sufficiently, the latter may be decolorised with charcoal, either at the same time as the lead acetate treatment or subsequently. As the charcoal absorbs a certain proportion of the dextrose, a correction becomes necessary, for which empirical values are given.

D. F. T.

**Colorimetric Estimation of Dextrose in Urine.** V. I. ISAACSON (*J. Lab. and Clin. Med.*, St. Louis, 1918, **3**, 289—294; from *Physiol. Abstr.*, 1918, **3**, 120).—A copper sulphate method, in which the unreduced copper is estimated after adding ammonia in a colorimeter against a standard.

S. B. S.

**Estimation of Dextrose in Urine.** C. H. HUGENHOLZ (*Pharm. Weekblad*, 1918, **55**, 609—614).—A comparison of the iodometric, polarimetric, and fermentation methods of estimating dextrose in urine. The first method is very accurate, the second gives slightly low results, and the values derived from the third method are extremely erratic.

A. J. W.

**Estimation of Sugar in Normal Urine.** STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1918, **34**, 195—201).—In this method, which permits of the estimation of traces of sugar accurately to within a few thousandths of 1%, the creatinine and polyphenols, and most of the total nitrogen and the glycuronic acid, are first removed from the urine by precipitation with a mercuric nitrate reagent, and the dextrose then estimated colorimetrically after treatment with picric acid. The necessary special reagents are prepared as follows. Mercuric nitrate solution, by adding slowly 220 grams of mercuric oxide to 160 c.c. of concentrated nitric acid until it has dissolved, then boiling, cooling, and adding 60 c.c. of 5% sodium hydroxide solution. It is made up to 1 litre and filtered. Picrate-picric acid solution, by adding 36 grams of picric acid and 400 c.c. of hot water to 500 c.c. of 1% sodium hydroxide solution and shaking until the picric acid has dissolved. It is cooled and made up to 1 litre.

To perform the estimation, 15 or 20 c.c. of the urine are placed in a 500 c.c. beaker, together with an equal volume of the mercuric nitrate solution, and, after mixing, solid sodium hydrogen carbonate is added until frothing ceases and an alkaline reaction to litmus paper is obtained. After filtering, the excess of mercury is removed by adding a pinch of zinc dust and a drop or two of concentrated hydrochloric acid. From 1 to 4 c.c. of the final filtrate (containing about 1 mg. of dextrose) are measured into a large test-tube graduated to indicate 12.5 and 25 c.c. Water is added if required to bring the volume to 4 c.c., and 1 c.c. of 20% sodium carbonate solution is run in, followed by 4 c.c. of the picric-acid solution. The mixture is heated in boiling water for ten minutes, cooled, diluted to the mark, and compared in a colorimeter with a standard solution similarly prepared from 1 mg. of dextrose in 4 c.c. of water or with a permanent standard of picramic acid or potassium dichromate solution. The former is prepared by adding 0.5 c.c. of 20% sodium carbonate solution and 15 c.c. of the picric-acid solution to 105 c.c. of exactly 0.01% picramic acid solution in 0.02% sodium carbonate solution and then diluting to 300 c.c. with water. To prepare the dichromate standard, dissolve 0.536 gram of potassium dichromate in 1 litre of water.

To estimate the fermentable sugar, a second estimation in the urine after fermentation is necessary. About 20 mg. of dextrose and a one-quarter cake of yeast are added to 25 c.c. of the urine. After mixing, it is allowed to remain in an incubator at 35–38° for eighteen to twenty hours. The clear urine is then decanted and the estimation of dextrose carried out as above. The difference between the two estimations gives the fermentable sugar.

H. W. B.

**Modification of the Lewis-Benedict Method for the Estimation of Dextrose in the Blood.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **34**, 203–207. Compare A., 1915, ii, 111).—The modification consists in adding the solution of picric acid in sodium picrate, employed in the estimation of dextrose in urine (see preceding abstract), instead of picric acid to the laked blood, which renders the subsequent evaporation unnecessary.

H. W. B.

**Sources of Error in the Estimation of Dextrose by the Colorimetric Picric Acid Method.** T. ADDIS and A. E. SHEVYK (*Proc. Soc. Exp. Biol. Med. New York*, 1918, **15**, 79).—The reddish-brown colour produced on heating dextrose, picric acid, and sodium carbonate varies with the temperature, duration of heating, and amount of carbonate present.

G. B.

**Inversion and Estimation of Sucrose.** A. R. ROSE (*Proc. Soc. Exp. Biol. Med. New York*, 1917, **15**, 16–17).—Heating for ten minutes at 100° with 2 volumes of saturated picric acid inverts the sucrose; then 1 vol. of 20% sodium carbonate

is added, and after a further twenty minutes' heating the total dextrose + levulose is estimated colorimetrically according to Lewis-Benedict. The amount originally present is estimated in a similar tube, in which the sodium carbonate was added before heating. The difference between the two tubes represents invert-sugar (compare preceding abstract). G. B.

**Estimation of Furfuroids (Furfurosans) in the Different Products of Beet Sugar Factories. I.** R. GILLET (*Bull. Assoc. chim. Sucr. Dest.*, 1917, **35**, 53—62).—It is known that other substances besides pentoses and pentosans yield more or less furfuraldehyde under the well-known conditions of distillation with hydrochloric acid. Chalmot has stated that sucrose yields not more than 0.2%, but the author, operating on 5—20 grams of pure sucrose, has obtained from 0.38 to 0.75% of furfuraldehyde under the Tollens-Counciler conditions of working. The method of procedure is described fully, and attention is directed to certain points which are of importance in securing uniform results. To prevent superheating, the distillation flask should not be immersed in the bath below the level of the liquid in the flask. The temperature of the bath should be such as to produce uniform distillation at the rate of 30 c.c. in twelve to fourteen minutes; when operating on 10 grams of sucrose, the author found it necessary to heat the bath to 155—160°, since at lower temperatures distillation was slow and the distillate was often cloudy, owing to the presence of an unknown, yellow substance in suspension. Great importance is attached to strict adherence to the prescribed method of replenishing the acid during distillation, exactly 30 c.c. being added as soon as 30 c.c. has distilled. In spite of attention to these and other details of procedure, it was found impossible to secure absolutely uniform yields of furfuraldehyde from sucrose. J. H. L.

**Colour Reaction for Ground Wood Pulp or the Incrusting Matters of Wood with Phenylhydrazine Hydrochloride.**

S. JENTSCH (*Zeitsch. angew. Chem.*, 1918, **31**, 72).—An aqueous solution of phenylhydrazine hydrochloride gives an intense orange-yellow coloration with raw wood fibre, which subsequently changes to a characteristic bright green on drying in presence of air; the appearance of the green colour is accelerated by suitable heating. Cotton and other pure cellulose fibres are stained only to a pale yellow, which changes to a characteristic light brown after drying. The above test for lignocellulose is stated to be sharper and more definite than the phloroglucinol-hydrochloric acid test. [See also *J. Soc. Chem. Ind.*, 365A.] J. F. B.

**New Reaction of Formic Acid and Hyposulphites.** E.

COMANDUCCI (*Boll. chim. farm.*, 1918, **57**, 101—102).—The presence of formic acid in a liquid may be detected by heating the latter gently with concentrated sodium hydrogen sulphite solution until gas bubbles begin to escape, the liquid being then cooled and

fresh, dilute sodium nitroprusside solution poured carefully on to its surface; a green or blue ring is thus formed, hydrogen cyanide being liberated at the same time. The blue precipitate,  $\text{Na}_4\text{Fe}_2(\text{CN})_9$ , results from the interaction of the nitroprusside and sodium hyposulphite, the latter being formed by the action of the formic acid on the sodium hydrogen sulphite (compare A., 1904, ii, 845).

T. H. P.

**Estimation of Lactic Anhydrides in Lactic Acid.** F. C. THOMPSON and KYOHEI SUZUKI (*J. Soc. Leather Trades' Chem.*, 1918, **2**, 115—121).—Lactide reacts completely in the cold with alkali hydroxide in ten minutes if the alkali is in considerable excess. No heating is therefore necessary in the analysis of lactic acid. Furthermore, the proportion of lactide present in lactic acid depends on the dilution and time of keeping, so that analytical results do not indicate the amount of lactide in a dilute solution used in technical practice, for example, in deliming hides. [See, further, *J. Soc. Chem. Ind.*, 343A.]. F. C. T.

**An Optical Method for the Estimation of Malic and Tartaric Acids in the same Solutions.** J. J. WILLAMAN

(*J. Amer. Chem. Soc.*, 1918, **40**, 693—704).—The method depends on the facts that uranyl acetate enhances the rotation of *l*-malic and *d*-tartaric acids, whilst ammonium heptamolybdate reverses the direction of the rotation in the case of *l*-malic acid, giving strongly positive solutions in each case. A chart is made connecting the rotations of solutions, containing up to 1% of the acids, activated by uranyl acetate on the one hand (the curves slope down from left to right) with those of solutions activated by ammonium heptamolybdate on the other (the curves slope up from left to right). The point of intersection of a given pair of curves will give, therefore, the number of grams of tartaric acid on the abscissæ and the proportion of malic acid on the ordinates.

The details of the method are based on Yoder's work on malic acid (A., 1911, ii, 1141) and further developments by Gore and others in America, which have been embodied in an official process (*J. Assoc. Off. Agric. Chemists*, 1916). An amount of the sample is taken which, judged by titration, will contain at least about 0.1 gram of either acid and not more than 0.6 gram of tartaric acid or 0.8 gram of malic acid. This is neutralised with *N*-ammonia solution, mixed with 2 vols. of 95% alcohol, filtered from pectins, and the filtrate slowly mixed with an excess of a 10% solution of barium chloride in 50% alcohol, and then made up to fourteen times the original volume with 95% alcohol. The precipitate is collected by centrifuging, boiled with water, mixed with 10 c.c. of 20% ammonium sulphate solution, the mixture is concentrated to about 80 c.c., cooled, mixed with 6 c.c. of glacial acetic acid, and diluted to 100 c.c. Two 25 c.c. portions of the clear solution, after centrifuging, are taken, mixed with 10 c.c. of an 8% solution of pure uranyl acetate and 10 c.c. of 10%

ammonium heptamolybdate respectively, left for three hours in the dark, and then polarised at about 20° in a 2-dcm. tube. If the molybdate solution becomes green through reduction, a drop of bromine water may be added.

J. C. W.

**Estimation of Fatty Acids in Butter Fat.** E. B. HOLLAND and J. P. BUCKLEY, JUN. (*J. Agric. Research*, 1918, **12**, 719—732).—Direct esterification of butter fat (with absolute alcohol containing hydrogen chloride or concentrated sulphuric acid), and subsequent fractional distillation of the resulting esters, affords a trustworthy method for the estimation of certain of the fatty acids. The following quantities of fatty acids were found in butter fat: hexoic acid, 1.36%; octoic acid, 0.975%; decaoic acid, 1.831%; lauric acid, 6.895%; myristic acid, 22.618%. Butyric acid (3.153%) and palmitic acid (19.229%) were estimated by difference, stearic acid (11.384%) by crystallisation, and oleic acid (27.374%) from the iodine number of the insoluble fatty acids. [See, further, *J. Soc. Chem. Ind.*, 846A.]

W. P. S.

**Test for Acetone in Urine.** M. WAGENAAR (*Pharm. Weekblad*, 1918, **55**, 57—60).—The presence of 0.5 mg. of acetone in 10 c.c. of urine can be detected by mixing the sample with a solution of acetic acid, tartaric acid, and sodium nitroprusside, and covering the liquid with a concentrated solution of ammonia. A coloration like that of permanganate solution is developed at the junction of the liquids.

A. J. W.

**Detection of Acetone in Urine.** P. BOHRISCH (*Pharm. Zeit.*, 1918, **63**, 173—174. Compare this vol., ii, 179).—The author finds that Legal's test is more sensitive than Lange's ring test, and mentions that Arends and Urban had shown in 1911 that it was not necessary for the sodium nitroprusside solution used in the tests to be freshly prepared.

W. P. S.

**Detection of Arbutin.** HANS SALOMON (*Ber. Deut. pharm. Ges.*, 1918, **28**, 138—139).—The tests commonly applied for arbutin in urine, for example, after the ingestion of bearberry leaf tea, are not specific to this substance.

D. F. T.

**Direct Estimation of Urea and Ammonia in Placenta Tissue.** FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1918, **33**, 381—385. Compare Sumner, A., 1916, ii, 655).—The methods of estimation recommended by the author are essentially those devised by Sumner (*loc. cit.*), the chief modification being the addition of potassium carbonate in a solid form to liberate the ammonia prior to aeration.

H. W. B.

**Estimation of Uric Acid in Urine and Blood.** D. G. COHEN TERVAERT (*Arch. Néerland. physiol.*, 1918, **2**, 337—345).—In the case of urine, the uric acid is precipitated by ammonium chloride as ammonium urate under conditions described by the author in detail. The precipitate is washed with ammonium chloride by

centrifugalisation, then dissolved in lithium carbonate solution, and the uric acid is estimated colorimetrically by Folin's phosphotungstate reagent in a solution made alkaline by sodium carbonate. In the case of blood, the proteins are separated by coagulation of the solution acidified by acetic acid, the filtrate is concentrated to a small bulk, and the uric acid is precipitated as urate and the amount estimated in a manner similar to that described for the estimation of uric acid in urine.

S. B. S.

**Estimation of Uric Acid in the Blood by Titration with Permanganate.**

J. LUCIEN MORRIS (*Proc. Amer. Soc. Biol. Chem.*, 1917, xxi; *J. Biol. Chem.*, 1918, 33. Compare A., 1917, ii, 279).—The uric acid from 20 c.c. of blood is isolated as zinc urate. It is then dissolved in hydrochloric acid and disodium hydrogen phosphate added until all the zinc is reprecipitated. A saturated solution of sodium hydrogen carbonate (25 c.c.), 10% potassium iodide (5 c.c.), and 0.5% starch solution (1 c.c.) are added, and 0.002*N*-permanganate run in from a burette until the blue colour of iodide of starch appears. In the slightly alkaline solution, the oxidation of the potassium iodide, and consequent production of the blue iodide of starch, does not occur until all the uric acid has been oxidised. The results are accurate to within 5%.

H. W. B.

**Homatropine and the Vitali Test.**

H. DROOP RICHMOND (*Analyst*, 1918, 43, 167—168).—Although the Vitali test serves to distinguish homatropine or its hydrobromide from atropine, hyoscyamine, or hyoscyne, it is untrustworthy when applied to homatropine sulphate, since the sulphuric acid in this salt causes the production of a violet coloration. In testing the sulphate, the alkaloid should be isolated and the reaction applied to it instead of to the original salt.

W. P. S.

**Microchemical Tests for Choline.**

N. SCHOORL (*Pharm. Weekblad*, 1918, 55, 363—369).—A description of the microchemical characteristics of double salts of choline hydrochloride with platinum chloride, gold chloride, mercuric iodide, bismuth iodide, and of the picrate and picrolonate.

A. J. W.

**Estimation of Creatinine and of Creatine in the Blood.**

ISIDOR GREENWALD and GRACE MCGUIRE (*J. Biol. Chem.*, 1918, 34, 103—118).—The new method consists in removing the blood-proteins by heat coagulation in dilute acetic acid solution, and then shaking with kaolin, which almost completely removes the creatinine, leaving the creatine unaffected. After filtration and concentration, the creatine is hydrolysed by hydrochloric acid and estimated by Folin's colorimetric method.

H. W. B.

**Detection and Estimation of Quinine in Blood and Urine.**

W. RAMSDEN and I. J. LIPKIN (*Ann. Trop. Med. Parasitol.*, 1918, 11, 443—464).—The thalleioquinine reaction is rendered more delicate



(1:40,000 with certainty) by adding to 10 c.c. of the quinine solution, feebly acidified with hydrochloric acid and shaken in a test-tube, one-tenth saturated bromine water drop by drop until the pale yellow colour is no longer instantly discharged (white background). At intervals of five seconds, lots of about 2 c.c. are poured into test-tubes containing one drop of concentrated ammonia. Finally, all ammonia solutions are mixed, and the green pigment is extracted with chloroform. The Herapath test may, with Christensen's reagent and a polarising microscope, be employed for the recognition of 1/500 mg. of quinine. Mayer's reaction (ordinarily 1:500,000) may be rendered twenty times as delicate by extracting the alkaloid with ether free from all traces of aldehyde or acetone, dissolving in saturated ammonium sulphate solution, and adding 1/100 volume of the reagent. Potassium triiodide (limit, 1:1,500,000) is less suitable, on account of the colour; phosphotungstic acid and bismuth potassium iodide are much less delicate.

Blood is boiled with ammonium sulphate, urine is precipitated with lead acetate and ammonium sulphate in the presence of acetic acid; in either case, after addition of ammonia to the filtrate, the quinine is extracted with ether free from ketones, the ether is evaporated, and the residue is dissolved in saturated ammonium sulphate solution (at least 10 c.c. for each mg. of quinine). The turbidity due to Mayer's reagent is compared nephelometrically with that in saturated ammonium sulphate solutions containing known amounts of quinine (gauged test-tubes in box with slit for illumination, dark-room, best dilution of quinine 200—300 c.c. per mg.). Thus 0.02—0.03 mg. of quinine in 5 c.c. of blood may be estimated with an error of less than 5%. Larger quantities of quinine (100 mg.) may be precipitated as periodide, from which the quinine is recovered with sodium hydrogen bisulphite and ether, so that it may be weighed or titrated. Gordin's volumetric method (*A.*, 1900, ii, 114, 777; 1907, ii, 487; 1902, ii, 186) is found to be accurate. G. B.

**Detection of Proteins by Bleaching Powder and Hydrochloric Acid.** ADOLF JOLLES (*Deut. med. Woch.*, 43, 1620—1621; from *Chem. Zentr.*, 1918, i, 303—304).—The test mentioned in the title is not sufficiently sensitive, and can be replaced by the following "three-tube test." The specific reagent contains 10 grams of mercuric chloride, 20 grams of citric acid, and 20 grams of sodium chloride in 500 c.c. of water. To three tubes are added 5 c.c. of filtered urine, to the first tube 1 c.c. of 30% acetic acid + 5 c.c. of the reagent; to the second, 1 c.c. of acetic acid + water, and to the third, water only. All tubes are made to contain the same volume of liquid. By comparing differences in the turbidities after remaining for ten minutes, it is possible to ascertain whether traces of proteins are present. S. B. S.

